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The Optical Dispersion of HCl in the Infrared

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(Received September 11, 1935)

There is, at present, a discrepancy of 162×10^{-6} between the temperature invariant part of the dielectric constant of HCl and the square of the index of refraction extrapolated to infinite wave-length; a difference which is more than 10 times the estimated uncertainty of the measurements, and which is usually assumed to be due to the contribution of infrared vibration bands to the index. In order to test the validity of the above assumption and also to investigate a seldom used method of determining the effective charge of molecules, the optical dispersion of HCl has been measured between 1 and 10μ. These measurements yield a value of $(1.00\pm0.05)\times10^{-10}$ e.s.u. for the effective charge of the rotator-vibrator; which shows, in agreement with measurements of intensity of absorption, that the contribution of the rotator-vibrator to n_∞ is much too small to explain the above discrepancy. Since the uncertainty in n_∞^2 as obtained from the refraction measurements is not more than 3×10^{-6}, this indicates that the uncertainty in the dielectric constant measurements must be somewhat larger than is ordinarily assumed. During the course of the investigation, it was discovered that the contribution of the pure rotation to the index of refraction was large enough to be measured with a fair degree of accuracy. Since most of the rotators are in excited states, these data furnish a quantitative check of the negative terms in the Kramers dispersion formula. They also furnish a new means of determining the electric moment; and the fact that the moment which is obtained agrees with that obtained from dielectric constant measurements indicates that the low absorption intensities observed by Czerny and by Badger must be in error.

INTRODUCTION

ACCORDING to ordinary dispersion theory, the temperature invariant part of the dielectric constant should be equal to the square of the index of refraction extrapolated to zero frequency. Van Vleck[1] has pointed out that for HCl there is a difference between the two which is far greater than the estimated uncertainty of the measurements. For example, the index of refraction measurements of Cuthbertson and Cuthbertson,[2] extrapolated from the visible, give for n_∞^2-1, $878\cdot10^{-6}\pm2\cdot10^{-6}$; while, from dielectric constant measurements, Zahn[3] obtains $1040\cdot10^{-6}\pm10\cdot10^{-6}$, a difference of $(162\pm12)\cdot10^{-6}$. The usual explanation for such discrepancies, that is, that they are due to the contribution of molecular vibration to the index, seemed in this case to be extremely improbable, since the absorption intensity measurements of Bourgin[4] indicate a contribution of the infrared vibration to n_∞ of only $1\cdot10^{-6}$. However, accurate measurements of absolute intensity are extremely difficult to make, and the wide range of values reported by various observers[5] makes a determination by a different method highly desirable.

It was Professor Van Vleck's suggestion that

[1] Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*.
[2] C. and M. Cuthbertson, Phil. Trans. Roy. Soc. **A213**, 1 (1913).
[3] C. T. Zahn, Phys. Rev. **24**, 400 (1924).
[4] D. G. Bourgin, Phys. Rev. **29**, 794 (1927); **32**, 237 (1928).
[5] For a review of intensity measurements up to 1926, see D. M. Dennison, Phil. Mag. **1**, 216 (1926).

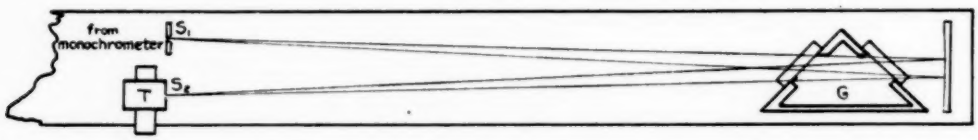

FIG. 1. The gas spectrometer. *T*, thermopile; *G*, gas prism. The distance from the gas prism to the slits is approximately 91 cm.

measurements of the index of refraction should be taken in the neighborhood of the rotation-vibration band. From these measurements it is possible to calculate the effective charge (for the vibration), that is, the rate of change of electric moment with internuclear distance; and consequently, from this, the contribution of the rotator-vibrator to n_∞. Since refraction measurements may be taken entirely outside the region of absorption, they are thus free from troublesome corrections due to nonhomogeneity of the light used. It was therefore believed that this type of measurement would provide a simpler and more accurate method of determining the effective charge than absolute intensity measurements, at least for molecules whose effective charge is fairly large.[6]

APPARATUS AND PROCEDURE

The apparatus was essentially the same as that used by Statescu[7] and by Wetterblad[8] for measurement of the index of refraction of CO_2. The method consists in measuring the change in deviation produced by a change in pressure in a hollow prism containing the gas being studied. Monochromatic light was obtained from a Wadsworth type rocksalt monochromator. A Nernst glower served as the source. Wavelengths were obtained from the calibration tables published by P. C. Cross.[9] Small errors in wavelength were not important in this work since the dispersion curve was nowhere very steep. The gas prism, a 90° hollow brass prism with holes 5 cm high by 6 cm wide, was provided with rocksalt windows 2 cm thick, the surfaces of which were sufficiently plane and parallel so that no troublesome corrections were necessary. These windows were pressed against rubber gaskets cemented to the brass by a mixture of beeswax and rosin. The joint between the salt and rubber was made vacuum tight by Lubriseal. Fig. 1 shows the arrangement and essential dimensions of the gas spectrometer.

The HCl generator and reservoir were all glass, except for the stopper in the generator flask which was rubber with a coat of wax on the bottom. The HCl was generated by dropping Merck's Reagent H_2SO_4 on Baker's Analyzed NaCl. The gas was condensed in a liquid-air trap. The whole system was kept evacuated by a Hyvac for some time before starting the reaction and during the generation. When an adequate supply of HCl had been condensed in the trap, it was shut off from the generator flask and the HCl was allowed to distill slowly into the gas prism and connections until a little more than the maximum pressure desired for the measurements had been reached. The stopcock between the prism and the first liquid-air trap was then closed, and the gas was condensed in a second trap which was connected through a stopcock to the gas prism so that the desired pressure could be developed in the prism and the stopcock then closed. After a run the gas was condensed in the trap.

An indication that reactions taking place in the gas prism were of little or no importance is furnished by the fact that, although the HCl was twice allowed to stand in the gas prism for about a month at a pressure of between one and two atmospheres, subsequent index determinations showed that there was no change greater than $0.5 \cdot 10^{-6}$ in the index. The slight apparent increase may have been error in measurement.

Gas pressures were read to one-tenth millimeter on an invar tape which was suspended between the two arms of a mercury manometer. The temperature of the gas prism was estimated to 1/100°C on a mercury thermometer which was checked at zero. Because of temperature

[6] Concerning the importance of effective charge measurements in the study of molecular structure, see R. S. Mulliken, J. Chem. Phys. **2**, 400; **2**, 712 (1934).
[7] J. Statescu, Phil. Mag. **30**, 737 (1915).
[8] T. Wetterblad, *Dissertation* (Upsala, 1924).
[9] P. C. Cross, Rev. Sci. Inst. **4**, 197 (1933).

variations in the room as well as the unreliability of the mercury thermometer, the temperature readings may have been in error by as much as 0.15°C.

A two junction, bismuth-tellurium, vacuum thermopile, rigidly mounted on the carriage of a comparator, served as a detector for the radiation. Several of the first runs were made with a pile equipped with a charcoal trap immersed in liquid air to maintain the vacuum. With this arrangement the determinations of image position showed small irregularities which were apparently attributable to small displacements of the comparator carriage caused by a variation in buoyancy due to evaporation of the liquid air. When a thermopile without a trap was used, it had to be repumped about once a month.

Changes of deviation were measured for changes of pressure of one to two atmospheres. To determine the position of the image, galvanometer readings were taken at definite space intervals as the thermopile was moved across the image. When 0.2 mm slits were used the reading was recorded every 0.050 mm, with 0.5 mm slits every 0.100 mm, and with 1 mm slits, every 0.200 mm. These readings were plotted, deflection against position, and the center of gravity of the resulting curve determined. This was averaged with the intersection of tangents drawn on opposite sides of the maximum. For some of the readings the direction of motion of the comparator was reversed. A comparison of the direct and reverse readings for the 0.2 mm slits indicates that the determinations of the image position are dependable to within 0.002 mm with large energies, and to about 0.005 mm with the smallest energy used. With 0.5 mm slits the uncertainty is about 0.004 mm and with 1 mm slits about 0.020 mm. The change of deviation for a change of two atmospheres in the HCl pressure was about 2.9 mm.

TABLE I. *Index of refraction of HCl.* Column V gives the method of observation. (1) One vacuum reading and one HCl reading, (2) vacuum readings before and after the HCl readings, (3) direct and reversed readings in each case with vacuum readings before and after the HCl readings.

WAVE-LENGTH (microns)	$(n_0-1)\times10^6$	p (mm)	SLIT WIDTH (mm)	METHOD OF OBS.
0.915	442.7	1495	0.5	1
1.06	442.6	1495	0.5	2
1.29	441.3	920	0.2	3
1.925	440.0	920	0.2	3
2.21	439.6	920	0.2	3
2.32	438.2	743	0.2	1
2.40	438.4	1506	0.2	1
2.48	438.4	743	0.2	1
2.53	438.3	920	0.2	3
2.56	437.4	1509	0.2	2
2.56	437.6	1506	0.2	2
2.645	436.5	743	0.2	1
2.73	437.2	1506	0.2	1
2.815	436.5	743	0.2	1
2.90	435.6	1509	0.2	1
2.90	435.7	1506	0.2	1
2.985	435.0	743	0.2	1
3.07	433.6	1506	0.2	1
3.15	433.0	743	0.2	1
3.23	426.3	1506	0.2	1
3.315	422.6	743	0.2	1
3.705	446.9	1506	0.2	1
3.705	444.3	1495	0.5	3
3.78	446.1	1509	0.2	1
3.855	442.4	1506	0.2	1
3.855	442.6	1495	0.5	1
3.855	443.4	1418	0.5	3
3.925	443.0	1509	0.2	1
3.995	441.4	1506	0.2	1
3.995	441.1	1495	0.5	3
4.06	439.8	1509	0.2	1
4.135	441.5	1506	0.5	1
4.135	440.3	1495	0.5	1
4.135	442.2	1418	0.5	3
4.40	439.2	1506	0.5	1
4.40	439.4	1495	0.5	2
4.59	438.5	1506	0.5	1
4.59	439.4	1495	0.5	2
4.59	439.7	1418	0.5	3
4.955	438.6	1506	0.5	1
4.955	437.8	1418	0.5	3
5.185	436.3	1495	0.5	2
5.755	437.7	1506	0.5	1
5.755	435.1	1495	0.5	2
6.055	435.6	1418	0.5	3
6.96	432.1	1307	1.0	3
8.00	431.1	1307	1.0	3
8.95	429.6	1307	1.0	3
10.20	428.1	1307	1.0	3*

* Poor data.

RESULTS

The relationship between change of deviation and index of refraction is given by the expression[8]

$$n-1-\Delta N=K(L-L_0)[1-K(L-L_0)/2].$$

In this equation ΔN takes care of the changes of index of the air surrounding the prism due to changes in temperature and barometric pressure occurring between the times the vacuum and high pressure readings were taken. L and L_0 are the positions of the slit image when the gas prism is full and evacuated, respectively. The constant K, which depends on the geometry of construction of the gas spectrometer, was determined by calibration with dry air. As standards the following values given by Wetterblad were used:

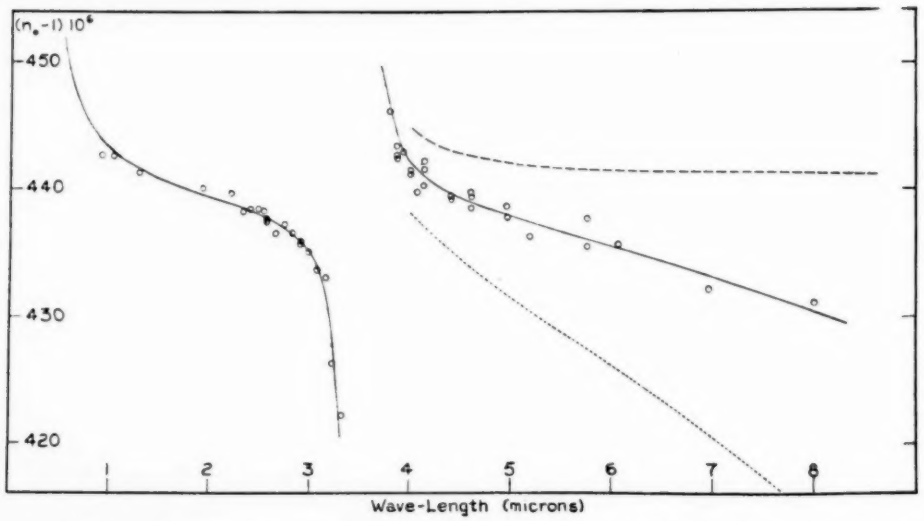

FIG. 2. Index of refraction of HCl as a function of wave-length. The continuous curve is the result of substituting $\epsilon = 1.00\times10^{-10}$ e.s.u. and $\mu = 1.18\times10^{-18}$ e.s.u. in the Kramers dispersion formula. The dotted curve represents the computed curve when the negative terms are omitted from the dispersion formula. The dashed curve indicates the course the curve would take if the pure rotation contributed nothing to the index of refraction.

$(n_0-1)10^6 = 288.78$ at 1.27μ; 288.12 at 2.32μ; 287.90 at 4.59μ; at 760 mm 0°C. In reducing from experimental to standard conditions and *vice versa*, the following relation was used:[8]

$$n_0-1=\frac{(n-1)(1+\alpha t)760}{p[1+\beta(p-760)]},$$

where α is the temperature coefficient of expansion and β is a factor introduced to allow for the fact that the index of refraction is not exactly proportional to the pressure. For air β is equal to $8\cdot10^{-7}$ (Wetterblad), and for HCl it is $1.6\cdot10^{-5}$. For HCl, since there were no tabulated values of β, this reduction was made by means of extrapolated pv data[10] and the Clausius-Masotti equation.

The values of n_0-1 are given in Table I and plotted in Fig. 2. In each case, all readings for one wave-length taken in one run are averaged. Column V indicates the method of observation: (1) One vacuum reading and one HCl reading, (2) vacuum readings before and after the HCl readings, (3) direct and reversed readings in each case with vacuum readings before and after the HCl readings. A smooth curve—not shown—was drawn to fit these points and the values of the index for particular wave-lengths were read from this curve. This curve was redrawn several times and the average values used in the following analysis.

[10] R. W. Gray and F. P. Burt, J. Chem. Soc. **95**, 1633 (1909).

CALCULATION OF ϵ AND μ

In the interpretation of the above data, contributions from three sources must be considered, the electrons, the vibrator-rotator, and the rigid rotator. The electronic contribution was obtained by extrapolation from the data of Cuthbertson and Cuthbertson reduced to standard conditions. In order to get best agreement with theory on both sides of the rotation-vibration band it was necessary to add $0.9\cdot10^{-6}$ to their values. This shift is reasonable since the values of the index of air used for calibration by Cuthbertson and by Wetterblad differed by approximately this amount. A constant shift such as was used means that the Cuthbertson data were actually used only to determine the rate of change of the electronic contribution with frequency.

In computing the contribution of the vibrator-rotator it was found that the use of a single frequency was unsatisfactory near the band. In order to consider the effect of the several frequencies in the band, the values of the ampli-

tudes as given by Oppenheimer[11] were substituted in the Kramers dispersion formula[12]

$$n^2-1=\frac{8\pi N}{\sum_l e^{-W_l^0/kT}}\sum_{l,\,l'}\frac{\nu(l';l)\,|P_E^0(l;l')|^2}{h[\nu(l';l)^2-\nu_0^2]}e^{-W_l^0/kT}. \tag{1}$$

The final result obtained for the contribution of the vibrator-rotator was

$$\Delta_{VR}(n^2-1)=\frac{N\epsilon^2}{3\pi m_{\text{eff}}\sum_0^\infty(2m+1)e^{-W_m/kT}}\sum_{m=1}^{\infty}\frac{mFe^{-W_m/kT}}{\nu(0,m;1,m-1)^2-\nu^2}+\frac{mF'e^{-W_{m-1}/kT}}{\nu(0,m-1;1,m)^2-\nu^2},$$

where ϵ = effective charge, ν = the frequency of the incident light, I = the moment of inertia of the unexcited molecule, ν_0 = the normal frequency of vibration,

$$F=[\nu(0,m;1,m-1)/\nu_0][1+4rm(1+\tfrac{5}{8}rm-\tfrac{3}{8}r)],$$
$$F'=[\nu(0,m-1;1,m)/\nu_0][1-4rm(1-\tfrac{5}{8}rm-\tfrac{3}{8}r)] \quad r=h/4\pi^2I\nu_0.$$

It was found sufficient to sum up to $m=12$. The frequencies and energy levels were obtained from the values given by Colby, Meyer, and Bronk.[13]

The contribution of the pure rotation was calculated by means of the Kramers dispersion formula in the form given by Debye (polar molecules). The same result may of course be obtained by substituting in Eq. (1) the matrix components of the electric moment of the rigid rotator. Since, in the region investigated, the rotational frequencies are always small compared with the frequency of the radiation used, ν_r could be neglected in the denominator. The contribution of the rotator may then be written

$$\Delta_R(n^2-1)=\frac{2N\mu^2}{3\pi I\nu^2\sum_0^\infty(2m+1)e^{-W_m/kT}}\sum_1^\infty(m^2e^{-W_{m-1}/kT}-m^2e^{-W_m/kT}),$$

where μ is the electric moment.

Considering all the contributions to the index of refraction, we then have $n_0^2-1=(n_0^2-1)_{C\&C}+f(\lambda)\epsilon^2+g(\lambda)\mu^2$. We thus have two disposable constants, ϵ and μ which are to be evaluated by comparison with the experimental results. These may be evaluated by successive approximations. We therefore assume a value of ϵ^2 and calculate μ^2 by comparison with the experimental curve, use this value of μ^2 and correct ϵ^2, continuing this process until the values obtained for ϵ^2 and μ^2 remain constant throughout the range of wavelengths available. In this calculation, the extrapolated values from Cuthbertson and Cuthbertson are shifted a small amount as indicated previously. The average values of ϵ^2 and μ^2 are obtained by weighting each value of ϵ^2 or μ^2 in proportion to the contribution to the index at that point, excluding the values at 9 and 10μ where the probable error in the experimental values of n_0-1 is large. The final results for ϵ and μ are

$$\epsilon=1.00\times10^{-10}\text{ e.s.u.};\ \mu=1.18\times10^{-18}\text{ e.s.u.}$$

These values of ϵ and μ were used in calculating the values of n_0-1 shown in Table II. This table also shows the agreement between the computed values and the experimental values used in the analysis. The smooth curve in Fig. 2 is plotted from the computed values to show the agreement with the experimental points.

Discussion

Although precise estimates of probable error are difficult to make for measurements such as these, it is possible, without any long rigorous analysis, to set rather definite limits to the uncertainty in the values of the effective charge and electric moment which have been calculated

[11] J. R. Oppenheimer, Camb. Phil. Soc. Proc. **23**, 327 (1926). See also, D. M. Dennison, Phys. Rev. **31**, 501 (1928). *Note added in proof:* The theory of the dispersion of a polar gas has recently been treated by C. Manneback, *Zeeman, Verhandelingen*, pp. 293–301.

[12] Reference 1, p. 361.

[13] Colby, Meyer and Bronk, Astrophys. J. **57**, 7 (1923).

TABLE II. *Experimental and computed values of* n_0-1 *for HCl.*

λ	A $\times 10^{-6}$	B $\times 10^{-6}$	C $\times 10^{-6}$	D n_0-1 (COMP.) $\times 10^{-6}$	E n_0-1 (EXP. CURVE) $\times 10^{-6}$	D−E $\times 10^{-6}$
1.0	443.41	− 0.11	− 0.17	443.13	442.7	+0.4
1.5	441.33	− .27	− .38	440.68	440.6	+ .1
2.0	440.61	− .59	− .67	439.35	439.6	− .2
2.5	440.27	− 1.28	− 1.05	437.94	438.1	− .2
2.6	440.22	− 1.50	− 1.14	437.58	437.7	− .1
2.7	440.18	− 1.81	− 1.23	437.14	437.2	− .1
2.8	440.15	− 2.22	− 1.33	436.60	436.5	+ .1
2.9	440.12	− 2.78	− 1.41	435.93	435.8	+ .1
3.0	440.09	− 3.63	− 1.52	434.94	434.8	+ .1
3.1	440.06	− 5.04	− 1.62	433.40	433.4	.0
3.2	440.04	− 8.06	− 1.73	430.25	430.5	− .2
3.3	440.02	−17.16*	− 1.84	(421.02)	421.8	− .8
3.7	439.95	+12.05*	− 2.31	(449.69)	446.4	+3.3
3.8	439.94	+ 8.45	− 2.44	445.95	443.0	+3.0
3.9	439.92	+ 5.99	− 2.58	443.33	443.0	+ .3
4.0	439.91	+ 4.87	− 2.70	442.08	442.2	− .1
4.1	439.90	+ 4.18	− 2.84	441.24	441.4	− .2
4.2	439.89	+ 3.71	− 2.98	440.62	440.8	− .2
4.3	439.88	+ 3.36	− 3.12	440.12	440.3	− .2
4.4	439.87	+ 3.09	− 3.27	439.69	439.8	− .1
4.5	439.86	+ 2.87	− 3.41	439.32	439.4	− .1
5.0	439.83	+ 2.23	− 4.21	437.85	437.8	+ .1
5.5	439.80	+ 1.92	− 5.11	436.61	436.4	+ .2
6.0	439.78	+ 1.73	− 6.08	435.43	435.1	+ .3
6.5	439.77	+ 1.65	− 7.11	434.31	434.0	+ .3
7.0	439.75	+ 1.57	− 8.28	433.04	432.9	+ .1
7.5	439.74	+ 1.51	− 9.51	431.74	431.9	− .2
8.0	439.74	+ 1.46	−10.80	430.40	431.0	− .6
9.0	439.72	+ 1.39	−13.67	427.44	429.4	−2.0
10.0	439.72	+ 1.34	−16.88	424.18	427.9	−3.7

A, $(n-1)$ by extrapolating data of Cuthbertson and Cuthbertson and adding 0.90×10^{-6}.
B, contribution of vibrator-rotator to index (computed).
C, contribution of rotator to index (computed).
* Too close to the absorption band to be reliable.

above. The average deviation of the experimental points from the computed curve is 0.34×10^{-6} on the short wave-length side of the vibration band and 0.47×10^{-6} on the long wave-length side. Considering the number of experimental points, a generous estimate of the probable uncertainty is then 0.1×10^{-6} on the short wave-length side and 0.2×10^{-6} on the long wave-length side. Inspection of Table II shows that if the readings are weighted as before, according to the size of the contribution, this corresponds roughly to an error of about 0.05×10^{-20} in the square of the effective charge or 0.025×10^{-10} in the effective charge. While this may be a little optimistic, we feel confident that this value of the effective charge cannot be in error by more than $\pm0.05\times10^{-10}$ e.s.u. As corroborative evidence there are the data obtained with the old thermopile, data which were not used in the final computations for the reason mentioned above. Three complete dispersion curves obtained with this pile gave a value for the effective charge of 0.95×10^{-10} on rough computation by ignoring the contribution of the pure rotation, and by using mainly the short wave-length side of the band. Taking account of the effect of the rotator would of course raise the result.

The value of the effective charge [$(1.00\pm0.05)\times10^{-10}$ e.s.u.] which we have obtained from measurements of the index of refraction, agrees with that obtained by Bourgin[14] from measurements of intensity of absorption. Other intensity measurements,[5] both earlier and more recent, giving values for the effective charge varying between 0.2 and $0.5\cdot10^{-10}$ cannot be reconciled with the refraction measurements. For example, the value of 0.48×10^{-10} reported comparatively recently by Bartholomé[15] would require a contribution to the index of refraction only one-fourth as large as is observed.[16] The results indicate, therefore, that for molecules with effective charges as large as that of HCl or larger, the refraction measurements probably afford a more accurate determination of the effective charge than do measurements of intensity of absorption. The prism method used in this work is, of course, unsatisfactory for the case of molecules (or modes of vibration) of much smaller effective charge, but interference refractometry is not limited in this way and should furnish sufficiently accurate results in such cases.

As has already been pointed out, the fact that the effective charge is as small as 1.00×10^{-10}, means that the contribution of the rotator-vibrator to n_∞^2 is about 2×10^{-6}, a contribution far too small to be of any help in removing the discrepancy of 162×10^{-6} between the value obtained by extrapolating optical index of refraction data and that obtained from dielectric constant measurements. The authors have had the benefit of numerous discussions with Dr. Zahn concerning the possible causes of this discrepancy. Dr. Zahn has made several suggestions concerning refinements in the interpretation of the dielectric constant measurements, but

[14] From Bourgin's data, Dennison computes $\epsilon=0.94\times10^{-10}$ while Bourgin obtains 0.86×10^{-10} e.s.u.
[15] E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).
[16] See, however, a discussion of Bartholomé's method by Kemble in J. Chem. Phys. **3**, 316 (1935).

rough estimates indicate that the contribution to n_∞^2 is invariably very small compared to the existing difference of 162×10^{-6}. The fact that von Braunmühl's[17] result for n_∞^2 differs from that of Zahn by 562×10^{-6} indicates that perhaps some source of error has been overlooked. It must also be kept in mind that, for the case of HCl, n_∞^2 is small compared with the total dielectric constant, so that a fairly small change in the dielectric constant data would be sufficient to bring about complete agreement.[1]

So far as the electric moment is concerned, a rough computation, such as that already made for the effective charge, indicates an uncertainty of about 0.09×10^{-36} in μ^2 or about 0.045×10^{-18} in μ. Eight percent would, therefore, be a generous estimate of the uncertainty in μ. The values of μ which seem to be most generally quoted in the literature are those of Zahn[3] and von Braunmühl[17] who obtained 1.034×10^{-18} and 1.18×10^{-18} e.s.u., respectively, using temperature variation of the dielectric constant. However, for the temperature invariant part of the dielectric constant, Zahn obtains 1040×10^{-6} and von Braunmühl obtains 478×10^{-6} while $n_\infty^2-1=880\times10^{-6}$. Consideration of the above measurements of the index of refraction together with the data of Cuthbertson and Cuthbertson shows definitely that the value $880\cdot10^{-6}$ for n_∞^2-1 cannot be in error by more than 3×10^{-6}, indicating that the uncertainties in the dielectric constant measurements must be somewhat larger than is generally assumed. If we use the value of n_∞^2-1 obtained from the refraction measurements and Zahn's dielectric constant we obtain 1.07×10^{-18} e.s.u. for μ, and, using von Braunmühl's dielectric constant, 1.12×10^{-18} e.s.u. If correction is made for the fact that the Langevin-Debye formula is not strictly applicable to HCl at room temperature,[18] these values are raised about 0.016×10^{-18}. The agreement between these values for μ and the one which we obtain from our dispersion measurements, $1.18\times10^{-18}\pm10\times10^{-18}$ e.s.u., must be considered satisfactory since the uncertainty of the different values is larger than the difference between them. The present knowledge of the magnitude of the electric moment of HCl is probably best expressed by $\mu=(1.11\pm0.05)\times10^{-18}$ e.s.u. Further index of refraction measurements, especially at longer wave-lengths, should reduce the uncertainty in μ to well below 5 percent.

The importance of the negative terms in the dispersion formula is shown in Fig. 2. The dotted line in the long wave-length region is obtained by considering only the positive terms in the rotational part of the Kramers dispersion formula, those corresponding to absorption, and neglecting the negative terms corresponding to induced emission. The dashed line indicates the course the curve would take if there were no contribution from the rotator. It will be noted that the contribution which would be obtained by using only the positive terms is about $2\frac{1}{2}$ times that by using the complete formula. The necessity for negative terms in the dispersion formula has, of course, already been demonstrated by the careful and extensive work of Ladenburg[19] and his associates on the dispersion of electrically excited gases. In their experiments, however, it was extremely difficult to determine the concentration of atoms in excited states, and furthermore, only a small fraction of the atoms could be maintained in these excited states. The conditions in the present work on HCl were more favorable for a quantitative check since most of the molecules were in excited rotational states, and since the distribution among the excited states was definitely determined by the temperature of the gas.

The fact that a reasonable value of μ is obtained from the contribution of the pure rotation to the index of refraction suggests that the anomalously low absorption intensities measured by Czerny[20] and by Badger[21] are to be explained by the fact that measurements of absolute intensity are extremely difficult to make, especially in the far infrared.[22]

The authors wish to thank Professor J. H. Van Vleck for suggesting the problem and for helpful advice on numerous occasions, and Professors C. E. Mendenhall and D. M. Dennison for helpful suggestions.

[17] H. J. v. Braunmühl, Physik. Zeits. **28**, 141 (1927).
[18] Reference 1, p. 197.
[19] R. Ladenburg, Rev. Mod. Phys. **5**, 243 (1933).
[20] Czerny, Zeits. f. Physik **34**, 227 (1926).
[21] Badger, Proc. Nat. Acad. Sci. **13**, 408 (1926).
[22] Professor Herzfeld has informed us that he has recently been able to show that the absorption intensities should be much smaller than has been calculated by older theories, but not enough smaller to remove the discrepancy.

On the Showers of Rays Which Produce Bursts of Cosmic-Ray Ionization

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(Received September 3, 1935)

An expression for the probability that a shower of a given number of rays will discharge a number of Geiger-Müller counters is derived and experimentally verified by observing the bursts of ionization in an ionization chamber and the simultaneously occurring discharges of three counters placed under the chamber. An estimate is made of the relative importance of the contributions of showers of various numbers of rays to the counting rate of counters placed out of line. The view that there is no sharp distinction between small showers as observed in cloud chambers and the very large showers which produce the bursts of ionization, or Stösse, in ionization chambers is emphasized. The results have a significant bearing upon the interpretation of counter experiments on showers.

IN the investigation of the showers of ionizing rays which are produced by cosmic radiation, many observers[1] have employed the simultaneous discharges of several Geiger-Müller counters placed out of line. Indeed, the first clear evidence of the existence of showers was obtained by means of them.[2] Now, only if showers consisted of an infinite number of rays, would the counters discharge simultaneously every time a shower occurred. The fraction of the number of showers which are recorded depends not only upon the geometrical configuration of the counters, but also upon the density of rays in a shower. In general, a small number of counters have been used in these investigations, and it has been natural to suppose that the counters are usually set off by a group of a small number of rays. An ionization chamber, on the other hand, will record all sizes of showers, but observations are limited to those sizes which are not obscured by the statistical fluctuations in the cosmic-ray ionization, i.e., to groups of rays containing numbers by no means small. It has been customary to imply that there is a sharp line of demarcation in frequency of occurrence and perhaps in other matters, between those sprays of small numbers of rays which have been usually referred to as showers, and the large groups commonly referred to as atomic bursts, or Stösse. It is proposed here to give evidence to support the view that, when the proper statistical considerations involving the probability of a counter discharge as a function of the number of counters, ray density, etc., are taken into account, the proper interpretation of the experiments so far performed lead to the conclusion that there is no marked discontinuity between small and large showers, but that all are represented in a more or less continuous gradation in size and are such as to suggest a family of phenomena intimately related as regards their origin and significance.

By making suitable assumptions, it is possible to arrive at an estimate of the probability that a shower of a given size will discharge a group of counters. Let us suppose that we have a source of showers and r counters placed under it. Let the number of rays in a shower be N, and suppose that these N rays are randomly distributed over a solid angle which includes all the counters. Let the *a priori* probability of one of the rays passing through the ith counter be p_i. The values of these *a priori* probabilities depend, of course, upon the conditions of the experiment: the positions of the counters, the solid angles subtended by the counters, etc. If $n_1, n_2, \cdots, n_r$ are the number of rays of the shower which pass through counters one, two, $\cdots$, r, respectively, then the probability of such a configuration of rays is the familiar multinomial distribution

$$\frac{N!p_1^{n_1}p_2^{n_2}\cdots p_r^{n_r}p_0^{n_0}}{n_1!n_2!\cdots n_r!n_0!}. \qquad (1)$$

n_0 and p_0 are defined by the relations $n_0+n_1+n_2+\cdots+n_r=N$, and $p_0+p_1+p_2+\cdots+p_r=1$, and refer to those rays which miss all r counters. If the counters are arranged so as to record a count when one or more rays pass through each

[1] B. Rossi, Zeits. f. Physik **82**, 151 (1933); E. Fünfer. Zeits. f. Physik **83**, 92 (1933); J. C. Street and T. H, Johnson, Phys. Rev. **42**, 144 (1932).

[2] B. Rossi, Physik. Zeits. **33**, 304 (1932).

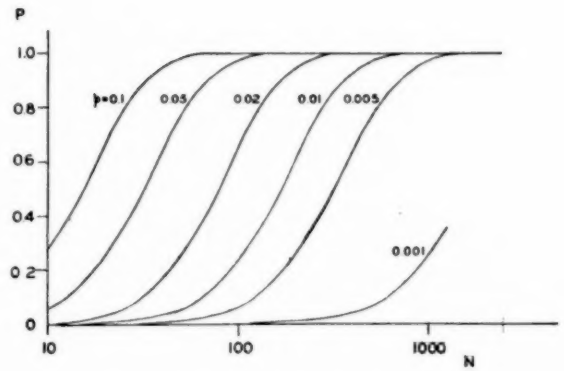

FIG. 1. The probability of the simultaneous discharge of three counters for various sizes of showers and *a priori* probabilities.

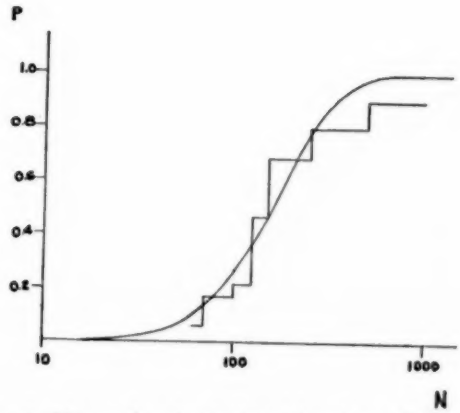

FIG. 2. Observed and calculated fractions of the number of bursts of ionization occurring simultaneously with a discharge of the counters.

counter simultaneously, the fraction of the number of showers of N rays which will produce a count is given by the summation of expression (1) over all values of $n_i \geqslant 1$, where $i \neq 0$. In the special case[3] when all the *a priori* probabilities, $p_1 \cdots p_r$, are equal, this sum may easily be found to be

$$\sum_{j=0}^{r} \frac{r!(-1)^j}{j!(r-j)!}(1-jp)^N. \qquad (2)$$

Fig. 1 shows how this probability varies with the number of rays in the shower for various values of p in the case of three counters.

It is possible to test this frequency formula experimentally by utilizing the fact that the sizes of bursts as measured in an ionization chamber are proportional to the numbers of rays in the corresponding showers. The fraction of the total number of bursts of ionization of any given size which occur simultaneously with the discharges of a group of counters suitably arranged is calculable through (2), and can also be measured experimentally, so that the principles underlying (2) can be tested. The apparatus used consisted of a spherical ionization chamber of magnesium immediately above which was placed enough lead shot to be equivalent to one centimeter of solid lead. The shot was contained in a square box whose side was approximately a diameter of the sphere. Under the sphere were placed three groups of three Geiger-Müller counters, the counters in each group being connected in parallel. The three groups were placed out of line with the center group below the other two, so that a ray passing through the sphere downwards could pass through only one group of counters. A simultaneous discharge of the three groups was made to flash a lamp, making a trace on the same photographic paper on which were recorded the bursts in the ionization chamber. The ionization chamber and its vacuum tube electrometer have been previously described.[4] The fraction of the number of bursts of ionization which were accompanied by a discharge of the counters was determined for bursts greater than 1.2×10^6 ions, in nitrogen at 14.5 atmospheres pressure. If we assume that the ionization was produced by rays of the ionizing power of high energy electrons (60 ions/cm at atmospheric pressure[5]), then we can determine the number of rays, N, in each burst which went through the sphere. The ratio of the mean solid angles subtended by the sphere and by one group of counters at the lead is the value of the *a priori* probability, p, associated with that group. This ratio was the same for all groups of counters and was equal to 0.01.

Fig. 2 shows how well the data obtained agree with expectation. In view of the fact that there are no arbitrary constants to be adjusted, and that some of the constants used in the reduction

[3] A more complete discussion of the derivation of these formulae is in preparation for publication in the Journal of The Franklin Institute.

[4] C. G. Montgomery and D. D. Montgomery, Phys. Rev. **47**, 429 (1935).

[5] W. F. G. Swann, Phys. Rev. **44**, 961 (1933).

of the data have a large uncertainty (the specific ionization of high speed electrons, for example) the agreement between theory and observation is excellent. This agreement amounts, then, to a verification of the assumptions made. These may be restated in the following way:

(a) The ionization in a burst is almost wholly produced by rays having the ionizing power of high energy electrons.

(b) The number of rays per unit solid angle is proportional to the total number of rays in the burst which pass through the chamber. (The fitting of theory to experiment did not necessitate the assumption that p is a function of N.)

(c) The rays are distributed at random.

Since the solid angle subtended by a counter group is 0.028, the density of rays in a shower giving 100 rays in the vessel is $100\times0.01/0.028$, or about 40 rays per unit solid angle.

Similar experiments have been performed, with other ionization chambers and other arrangements and numbers of counters, which, although the data are more fragmentary, agree with expectation as well as the experiment here described.[6] It is to be noted that the above method of measuring the experimental probability that a burst of ionization of any given size will be accompanied by a discharge of the counters gives an average value taken over all regions of origin of the showers and directions of the line of symmetry of the shower particles. However, since only rays which have passed through the ionization chamber are recorded either by the counters or by the electrometer, the results are largely independent of the distribution in angle of the showers, and of their place of origin. In all the above considerations the fraction of the time during which the counters were insensitive was assumed to be negligible. If this assumption were eliminated, and the necessary small correction made, it would take the form of a constant factor, slightly greater than unity, multiplying all the experimental probabilities and would thus tend to improve the agreement with theory.

In the foregoing section we have given an answer to the question, "How many bursts of ionization of a given size are accompanied by a discharge of the three counter groups?" Let us now invert the question and ask, "What fraction of the total number of the simultaneous discharges of the counters is produced by showers of a given size?"

If showers containing N rays occur at the rate of $R(N)$, and if the probability of a shower being recorded by some arrangement of counters is $P(N)$, then the counting rate, C, will be given by

$$C=\sum_{N=1}^{\infty}R(N)P(N).$$

Since we know $R(N)$ from the ionization data, it should be possible to compute the total counting rate of the counters used in the experiment described above, and compare it with the observed rate. It is necessary to know the distribution function, R, for values of N smaller than it is possible to observe in this chamber, and these values must be obtained by extrapolation.

Fig. 3, curve A, shows the observed distribution curve, $R(N)$, plotted on a logarithmic scale. The number of single rays passing through the chamber in unit time (one hour) is 1.48×10^5.[7] From this, the number of showers of two, three, etc. rays are obtained by using the cloud chamber observations[8] of the relative frequency of these small showers, and are also plotted. All these data are satisfactorily represented by a relation of the form $R=A/N^4$, which is a straight line on our diagram. There is no evidence here that there is any fundamental distinction to be made between large and small showers. This method of extrapolation gives not only a satisfactory representation of the frequency of large and small showers, but also reasonable values for the ionization produced by showers (20 percent of the total ionization) and the size of the observed fluctuations in ionization (the standard deviation computed for single rays must be multiplied by 1.2 to correct for showers). A frequency distribution function of this same form also satisfactorily represents the experimental distributions in various other ionization cham-

[6] W. F. G. Swann and C. G. Montgomery, Phys. Rev. **44**, 52 (1933); W. F. G. Swann, J. Frank. Inst. **218**, 173 (1934). Report on the Work of the Bartol Research Foundation, 1933–1934.

[7] J. C. Street and R. H. Woodward, Phys. Rev. **46**, 1029 (1934).

[8] C. D. Anderson, Phys. Rev. **44**, 406 (1933).

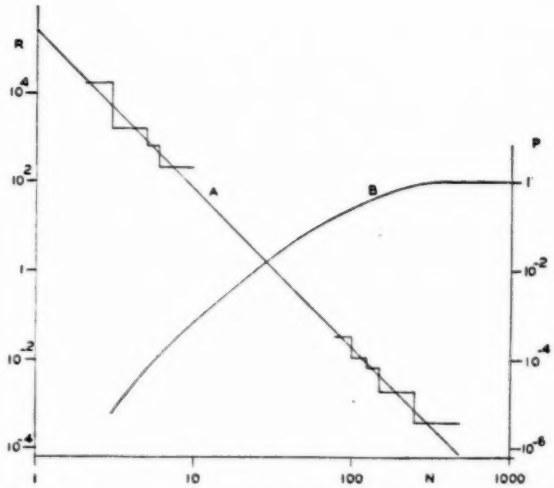

FIG. 3. Curve A, frequency distribution of showers, $R(N)$. Curve B, probability of a count, $P(N)$.

bers, including one experiment in which showers of from ten to one thousand rays were measured, and whose rates of occurrence varied over a factor of 10^5. Curve B, Fig. 3, is the function $P(N)$. The scale of ordinates is at the right. The function PR, obtained by multiplying the above functions, increases from zero, for two-ray showers, to a maximum for showers of eight or nine rays and then falls monotonically as N increases. The counting rate due to showers greater than 60 rays is the observed rate of occurrence of counts coincident with bursts of ionization, *viz.*, 0.9 per hour. The total counting rate computed from these data is 2.5 per hour. The observed counting rate was 5.5 per hour. In view of the large range of extrapolation, this agreement is quite satisfactory. Indeed, we should expect the observed counting rate to be greater than the rate computed in this manner, since no account has been taken of the showers which set off the counters without passing through the chamber. Further, we find that the contribution of showers below ten rays (0.4 per hour) is of the same order of magnitude as the contribution of showers greater than 100 rays, and that more than half of the counts are caused by showers greater than 30 rays. This situation is not a consequence of the particular arrangement of counters considered here, but holds for most cases where counters have been used to investigate showers. Thus the phenomena which counters record are, in general, quite complicated ones.

The importance of the foregoing considerations is attested by the fact that, in investigating showers, it has been customary to use two or three counters, and regard their simultaneous discharges as evidence of the occurrence of doubles, triples, etc., at the same time regarding any discharges produced by large showers or Stösse as of such rare occurrence as to be negligible, or at any rate to figure only as a correction. We must now realize that the rarity of occurrence of the large showers is largely compensated by the large chance which they have of operating the counters, in comparison with the much smaller chance of operation that three-ray showers have, for example. The net result is that the number of discharges of the counters produced by the large showers is comparable with the number produced by those which it is the object of the experiment to measure.

It has also been a common practice, when using counters to investigate showers, to correct for the showers observed when no shower producing material is present by subtracting the "zero" counting rate from all the others. This is, of course, a valid procedure only when the distribution functions, $R(N)$, combine linearly. It has been previously pointed out[9] that this is not true in general, and that one piece of matter can affect the showers from another piece not only by an absorption process, but also by producing additional ionizing rays. An inspection of the data on "transition" phenomena shows that this is quite a general property, and its effect must be carefully considered in drawing conclusions from counter data.

The authors wish to express their appreciation to Professor W. F. G. Swann for his interest, advice, and criticism during the progress of this work, which grew out of joint investigations with him referred to in earlier publications. The authors also wish to acknowledge the financial support of the American Philosophical Society in carrying out this investigation.

[9] C. G. Montgomery, D. D. Montgomery and W. F. G. Swann, Phys. Rev. **47**, 512 (1935); C. G. Montgomery, Phys. Rev. **45**, 62 (1934).

The Radioactivity Induced in Oxygen by Deuteron Bombardment*

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An induced radioactivity of half-life 1.16 minutes has been observed after the bombardment of oxygen or its compounds by 3 MV deuterons. The disintegration particles were observed to be positrons. Chemical tests showed that the active substance was an isotope of fluorine. The probable reactions are therefore:

$$O^{16}+D^2=F^{17}+n^1; \qquad F^{17}=O^{17}+e^+.$$

A product of the same properties was already known to be induced in nitrogen under α-particle bombardment. The activation function of oxygen has been measured by collecting radioactive recoil atoms at several points along the path of the deuteron beam when it is passing through an atmosphere of oxygen. The excitation curve drops very rapidly and goes to zero at about 2 MV deuteron energy. This is best accounted for by assuming that energy disappears in this reaction, and that the energy of reaction is the negative of the threshold energy. By correcting for recoil, $Q=-1.8$ MV. To confirm this estimate of the energy of reaction, the maximum angle between the direction of the deuteron beam and the paths of the radioactive recoil atoms has been measured. A piece of optical quartz (SiO_2) was bombarded at a glancing angle by a narrow beam of deuterons, and radioactive recoil atoms were collected on a cylindrical strip of copper which was placed about the target. The maximum angle of recoil was found to be about 30° which corresponds to $Q=-1.3$ MV. The agreement with the value, -1.8 MV found previously, is within the errors of the measurements. In order to check the method the same experiment was performed with a graphite target; the longer half-life of the active material made possible a more accurate measurement. The maximum angle of recoil was found to be 42° for the activation of carbon; this corresponds to $Q=-0.1$ MV for the reaction $C^{12}+D^2=N^{13}+n^1$. This agrees reasonably well with the experimental value of Q found by Tuve and Hafstad and with the value of Q which is deduced from maximum energy of the positrons from N^{13} and the range of the protons which are emitted when carbon is bombarded by deuterons.

INTRODUCTION

NEGATIVE results have been obtained in most of the previous experiments in which oxygen has been bombarded by charged particles. No certain effects have been observed with α-particles or protons of the highest available energies. Oliphant and Rutherford,[1] and Cockcroft and Walton[1] have shown that deuterons lead to the emission of a short proton group, but McMillan and Livingston[2] found no detectable radioactivity when oxygen was bombarded with deuterons of 1.9 MV energy. The reason for this abnormally high stability of the oxygen nucleus has not been clearly understood. The work to be described in this paper shows, however, that in at least one of the cases cited above, the possible reaction did not occur simply because the energy of the bombarding particle was not sufficient to compensate for that lost in the reaction: oxygen may be activated by bombardment with very high energy deuterons, but this activation occurs only above a well-defined threshold. An independent estimate of the energy of this reaction shows an energy loss approximately equal to the threshold energy of the deuteron.

ESTABLISHMENT OF THE REACTION

The first evidence for induced radioactivity in oxygen was found in some experiments on radioactive silicon. When a piece of quartz was bombarded in an atmosphere of oxygen with 3 MV deuterons, an activity was found which was much stronger than any which have been observed in pure silicon. Activities of the same half-life have since been found after the bombardment of iron oxide, water, and gaseous oxygen. A logarithmic plot of the decay curve of the radioactive substance is shown in Fig. 1; measurements of the half-life give a reproducible value of 1.16 minutes.

The tracks of the particles emitted by this substance have been observed in a Wilson cloud chamber.[3] The direction of curvature of the tracks in a magnetic field shows that they are positrons. The probable reactions may be written:

* A preliminary report on these experiments was given at the Los Angeles Meeting, June 10, 1935.

[1] See Cockcroft and Walton, Proc. Roy. Soc. **A144**, 704 (1934).

[2] McMillan and Livingston, Phys. Rev. **47**, 452 (1935).

[3] I am indebted to Dr. Kurie for the use of his apparatus in this experiment.

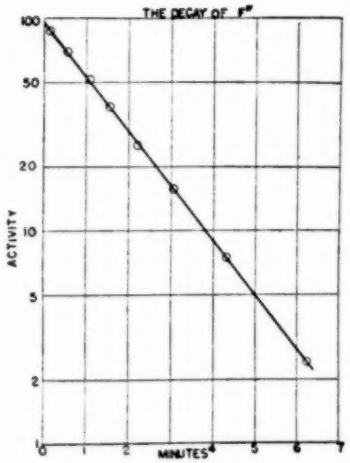

FIG. 1. A logarithmic plot of the decay of F^{17}; the half-life of this substance is found to be 1.16 minutes.

$$O^{16}+D^2=F^{17}+n^1, \quad (1)$$

$$F^{17}=O^{17}+e^+. \quad (1a)$$

The identity of the active substance was established by a chemical separation. A small amount of water was bombarded behind an aluminum window of 4 mm stopping power. The water was then rinsed into a boiling solution of potassium fluoride which also contained small amounts of aluminum chloride and nitric acid. Calcium chloride was then added and the precipitate, calcium fluoride, filtered out; active aluminum from the window remained in the acid solution. The precipitate showed a large activity which decayed with the expected period.

A radioactivity of the same properties has been observed by Wertenstein[4] and others after the bombardment of nitrogen by α-particles. In this case the probable reactions are

$$N^{14}+He^4=F^{17}+n^1, \quad (2)$$

$$F^{17}=O^{17}+e^+. \quad (2a)$$

THE EXCITATION FUNCTION OF OXYGEN

It will be observed that the reaction giving rise to F^{17} is analogous to the well-known reactions:[2]

$$C^{12}+D^2=N^{13}+n^1, \quad (3)$$

$$N^{14}+D^2=O^{15}+n^1. \quad (4)$$

However, the excitation function for oxygen must be quite different from those of the neighboring elements since the above reactions will go at very low bombarding energies while Livingston and McMillan could not activate oxygen with 1.9 MV deuterons. It would seem, then, that a study of this abnormal excitation should be of considerable interest.

The excitation curve for oxygen has been determined with some care while approximate curves have been obtained for carbon and nitrogen for purposes of comparison. The measurements were made by passing the deuteron beam through a gas containing the element to be studied and collecting radioactive recoil atoms at various points along the path of the beam. The activity was collected on a series of large mesh copper screens which were placed perpendicularly to the beam so that it passed through each one of them in turn. The screens were spaced about 6 mm apart. The activity collected on a screen should be proportional to the excitation of the element in question by deuterons of the energy which they have as they pass the screen. The experiment was carried out in a space about 3 cm long while the total range of the beam was more than 10 cm; since the experiments were run at atmospheric pressure, it was necessary to replace some of the earlier screens by foils of known stopping power in order to carry the measurements to lower energies.

The activities deposited on the screens were high enough to allow the exposure and measurement of about six screens at one time. The decay of the activity on each screen was determined, and, in this way, activities due to contaminations could be eliminated. In Fig. 2, the results of these measurements on carbon and oxygen are shown. A few points on the nitrogen excitation curve were obtained, and it was shown to be similar to that of carbon. The gases used were carbon dioxide and free nitrogen and oxygen. The short period activity which would arise from the oxygen in carbon dioxide was allowed to die out before the longer lived activity from carbon was measured.

The most serious error in these measurements is caused by the interference of the screens with the beam; if any large fraction of the beam is stopped by the screens, the excitation curve will

[4] Wertenstein, Nature **133**, 564 (1934); Ellis and Henderson, Proc. Roy. Soc. **A146**, 206 (1934).

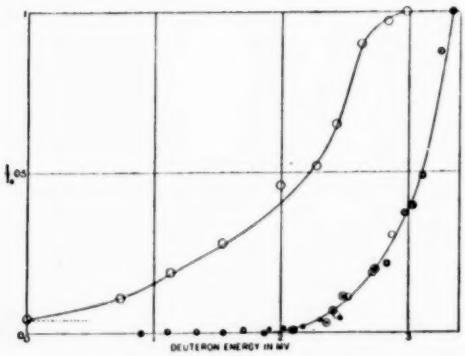

FIG. 2. The excitation curves of oxygen and carbon. In the oxygen curve (right) the five points along the axis shown as heavy circles are those for which diffusion has been eliminated. Diffused activity has not been eliminated on any of the points on the carbon curve (left) and there is consequently a background, shown as a dotted line, which must be subtracted from the curve.

drop too rapidly. The screens were lined up as well as possible to prevent any screen except the first from stopping deuterons, but, since the deuteron beam was curved by the strong magnetic field of the ion accelerator, the alignment could not be very precise. However, the importance of the errors arising from this cause may be determined by changing the spacing of the screens. If the experiment is performed twice under the same conditions except that all six screens are in place in one case and only the first and last screens are in place in the other, the total number of deuterons stopped by the screens should be much higher in the former case; the weakening of the beam may be measured by plotting the results of the two experiments together. If the two curves coincide at all points after they have been fitted at one point, the error under investigation is unimportant. In the actual measurements, the effective spacing was changed by introducing foils between two of the earlier screens. Many exposures were made with oxygen with great differences in the effective spacing. It will be seen in Fig. 2 that all of the several runs follow the same curve independent of the spacing. The activity found on the first screen in each run was found to be reproducible but evidently too high. This is to be expected since this screen certainly stops 10 percent of the beam. For this reason, the activity of the first screen is not shown in the curve.

A correction for the variation of the range of the recoil particles with the deuteron energy might be applied since this range determines the effective target thickness in these experiments. However, the correction is not important for the oxygen curve.

It was shown very simply that diffusion of the active gas from one region to another had little effect on the curve where the activity was large. The activity of a screen was measured on both sides; the side of the screen which was struck by the beam was found to be twice as active as the other. This is about the difference in intensity to be expected if a sheet of the same thickness as the wires of the screen were placed over the active substance. It is evident, then, that nearly all of the activity on the screen is on the "front" side. Since the recoil atoms in both the carbon and the oxygen reactions are driven only in the forward direction (see the later experiments) nearly all of the activity must be deposited on the screens by recoil. However, where the activities are very low, diffusion of the activity undoubtedly becomes important. Below 2 MV on the oxygen curve, the very small activities which are found show no definite trend and are probably due entirely to diffusion. In order to eliminate diffused activity, the five points at the lowest energy were taken with an aluminum foil of 49 mm stopping power absorbing most of the energy of the deuterons; it will be noticed that the activities of this set of points are decidedly lower than the next higher set where most of the stopping power was oxygen, and there was, consequently, more activity to diffuse. It seems safe to say, then, that there is no detectable excitation of oxygen by deuterons of less than 2 MV energy.

The excitation curve of carbon which is shown in Fig. 2 was obtained from a single set of measurements and is by no means precise. However, the general trend of the curve has been checked by an independent method. Since this curve was obtained only for comparison with that of oxygen, the corrections mentioned previously were not made. Since diffusion was not eliminated, there is a background due to it which must be subtracted from the curve. A few points on excitation curve of nitrogen have been obtained; they follow the carbon curve very closely.

The Energy of Reaction and the Mass of F^{17}

The obvious explanation for the very great difference between the excitation curve of oxygen and those of carbon and nitrogen is that a large amount of energy is lost in the oxygen reaction so that the energy deficiency must be made up by the deuterons before any excitation occurs. There can be no question that the deuterons are entering the oxygen nucleus, since disintegration protons have been obtained from oxygen under bombardment by deuterons of much less than 2 MV energy.[5] How accurately this energy loss may be estimated from the excitation curve is a difficult question. In the last section it was shown that the excitation curve of the reaction shows an experimental threshold in the neighborhood of 2 MV bombarding energy. However, the real threshold which corresponds to the loss of energy in the reaction will lie somewhat below this energy. In the case of the excitation of carbon, which is closely analogous to that of oxygen, the real threshold (i.e., the energy of reaction) is about zero (see later experiments) while the experimental threshold as found by Hafstad and Tuve[6] and by Cockcroft, Gilbert and Walton[7] is below 0.4 MV. This difference is due, at least in part, to the potential barrier of the nucleus which is penetrated with great difficulty by charged particles of low energy. In the case of oxygen, it is evident that, in the neighborhood of the experimental threshold, the potential barrier is being penetrated with relative ease since the reaction $O^{16}+D^2=O^{17}+H^1$ occurs at comparatively low bombarding energies; it would be expected then that the difference between the real and experimental thresholds would be less than for carbon, because of the relative ineffectiveness of the potential barrier. If then we take the real threshold as equal to 2 MV, we are certainly not high by more than 0.4 MV. Correcting for recoil, the energy of disintegration, $Q=(8/9)2.0=-1.8$ MV.

The excitation curve for the reaction: $N^{14}+He^4=F^{17}+n^1$ has been determined by Haxel.[8] A threshold was found in this excitation curve at an α-particle energy of 6 MV. This threshold may be taken as a measure of the energy of reaction by the same arguments as are used above. The α-particles are known to be entering the nucleus below the threshold since protons are emitted at considerably lower bombarding energies. Then from the threshold energy $Q=-(7/9)6=-4.7$ MV. The same kind of an error is made here as in the previous case.

The consistency of these assumptions may be checked by calculating the mass of F^{17} from the two reactions. From the oxygen-deuteron reaction:

$$F^{17}=16.0000+2.0142-1.0083+0.0019=17.0078. \quad (1')$$

From the nitrogen-α-particle reaction:

$$F^{17}=14.0080+4.0034-1.0083+0.0050=17.0081. \quad (2')$$

The check is well within the error in the masses. The masses are taken from the paper of Oliphant, Kempton and Rutherford[9] except for N^{14} for which the old Aston value is used. The use of the new masses of Aston[10] or those generally accepted last year give satisfactory checks although the absolute values obtained differ considerably. The agreement of the two calculated values is independent of the mass of the neutron and of a systematic error in the estimates of the energies of reaction. The check does show, however, that the interpretation of the experiments is consistent.

The Angle of Recoil of Active Atoms

An attempt was made to detect the neutrons given off during the excitation of oxygen by measuring the neutron induced activity in silver. However, no effect was found which was large enough to show against the high neutron background of the apparatus. The value of the energy of reaction obtained from the excitation curve cannot, then, be checked by studying hydrogen recoils of the neutrons, but it is possible to study the radioactive recoil nuclei which are formed at the same time as the neutrons. Since these neutrons are not very energetic, they are not able to drive the recoil nuclei in the backward direc-

[5] Cf. 1. The bombarding energy used by these workers was less than 1 MV.
[6] Hafstad and Tuve, Phys. Rev. **47**, 506 (1935).
[7] Cockcroft, Gilbert and Walton, Proc. Roy. Soc. **A148**, 225 (1935).
[8] Haxel, Zeits. f. Physik **93**, 400 (1935).
[9] Oliphant, Kempton and Rutherford, Proc. Roy. Soc. **A150**, 241 (1935).
[10] Aston, Nature **135**, 541 (1935).

tion but simply deviate them from the path of the deuteron beam by an angle dependent on their energy.

The velocity of the recoil nucleus, V_R, may be found from the equations of conservation of energy and momentum:

$$V_R=\frac{1}{M_n+M_R}M_D V_D\cos\theta\pm\frac{M_n}{M_n+M_R}\left\{\frac{2M_D}{M_n^2}E_D\cos^2\theta+2\frac{M_n+M_R}{M_R M_n}\left[Q+E_D\left(1-\frac{M_D}{M_n}\right)\right]\right\}^{\frac{1}{2}}. \quad (5)$$

M, V and E are mass, velocity and energy, respectively, and the subscripts D, n and R refer, respectively, to the bombarding particle, the emitted particle, and the recoil nucleus; θ is the angle between the path of the deuteron and that of the recoil atom; and Q is the kinetic energy which appears in the reaction. The expression under the radical reduces to the form:

$$(1-\beta^2\sin^2\theta)^{\frac{1}{2}},$$

where $\beta^2=\dfrac{2M_R E}{(M_R+1)\{[(M_R-1)/(M_R+1)]E+Q\}}$.

If $\beta^2>1$ there will be an angle between 0° and 90° above which this term becomes imaginary. For reactions in which $Q<E$, approximately, there will be a maximum angle of deflection given by the equation

$$\sin^2\theta_{\max}=1/\beta^2$$

or $$Q=E\left(\frac{2M_R}{M_R+1}\sin^2\theta_{\max}-\frac{M_R-1}{M_R+1}\right). \quad (6)$$

This maximum angle should be sharply defined and accurately measurable; the value of Q obtained from it is independent of range velocity data which are not very accurately known for heavy particles. The result is, also, largely independent of the number of charges on the recoil atoms and of their velocity after emerging from the target.

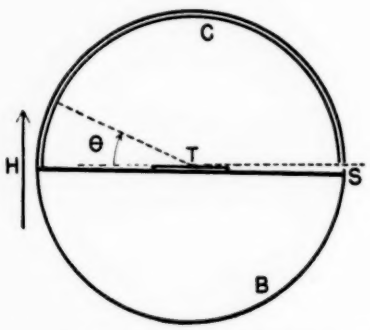

FIG. 3. Apparatus for measuring the angle of recoil of radioactive atoms. The tube is 4 cm in diameter.

The maximum angle of recoil was measured with the apparatus shown in Fig. 3. The deuteron beam enters the brass tube, B, through the slit, S, and strikes the target, T, at a glancing angle. The radioactive recoil atoms are collected by a metal strip, C, which lines the inside of the tube B. This arrangement collects only those atoms of which the component of velocity perpendicular to the beam is approximately parallel to the strong magnetic field H which must be present in this type of ion accelerator. The field cannot therefore change the angle θ greatly although very slow or highly charged recoil atoms are considerably bent by the magnetic field. In performing the experiment, the target was bombarded in vacuum for several half-lives of the substance. The metal strip was removed, cut into small slices perpendicular to its long side, and the activity of each piece was measured on the electroscope. The decay of some of the pieces was checked to be sure that the activity was due to the element studied.

THE ENERGY OF REACTION IN THE ACTIVATION OF CARBON

Because of the convenient half-life (10.4 minutes) and the great intensity of the activity of carbon, the first experiments were performed on a graphite target. Fig. 4 shows a histogram of the distribution of activity between 12° and 100°. The distribution between 80° and 180° was studied carefully in another experiment and was found to be constant within the accuracy of the measurements. This small activity might be ascribed to a weak group of neutrons of energy greater than $2E$, but the lack of any apparent dependence of the distribution on the angle leads one to suspect that the activity is due to some other cause. Since the total activity found in this

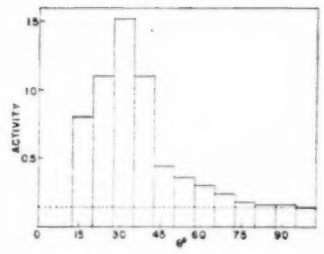

FIG. 4.

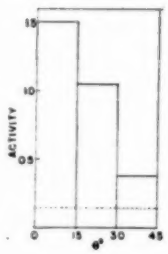

FIG. 5.

FIG. 4. The angular distribution of the recoil atoms from carbon. The dotted line is a background probably due to diffused activity.

FIG. 5. The angular distribution of the recoil atoms from carbon. The dotted line is again a background.

region is less than one percent of that of the graphite target, it is probable that enough charged atoms could escape from the target at thermal velocities and stick to the surrounding surfaces to account for the observed activity. The dotted line in Fig. 4 shows the magnitude of this background which should be subtracted from the observed activities at smaller angles. After correcting for the background, a "tail" of low intensity remains between 42° and 80°. Since cloud chamber experience shows that about ten percent of the observed tracks of heavy atoms are perceptibly bent, it seems likely that the tail is composed of atoms which have been scattered from the intense beam which is found at smaller angles. Scattering is nearly as probable in this experiment as in a cloud chamber since most of the recoil atoms must travel an appreciable distance below the surface of the target before they emerge. The rate of fall of the curve in this region is not inconsistent with the assumption that the active atoms have been scattered.

Taking the maximum angle of recoil as the high angle side of the region of intense activity, $\theta_{max}=42°$, and $Q=-0.1$ MV. This value of Q may be compared with one calculated from the reactions:

$$C^{12}+D^2=C^{13}+H^1+Q_1, \tag{7}$$

$$N^{13}=C^{13}+e^+ +(e^-)+Q_2; \tag{7a}$$

combining these with the reaction

$$C^{12}+D^2=N^{13}+n^1+Q \tag{3}$$

we obtain $$Q=H^1-n^1-e^+-(e^-)+Q_1-Q_2. \tag{8}$$

Q_1 may be calculated from the data of Henderson, Livingston and Lawrence;[11] if it is assumed that no γ-rays accompany the protons, $Q_1=2.65$ MV. Q_2 may be taken as 1.3 MV, the maximum energy of the positrons from N^{13}, as measured by a number of workers.[12] Using the same masses as before we obtain $Q=0.1$ which is in excellent agreement with the measured value. The two values of Q obtained here are in reasonably good agreement with the measurements of Tuve and Hafstad[13] who find $Q=0.25$ MV for this reaction. The agreement of these three values of Q seems to be a good check on the reliability of this method; however, the measurements described here leave open the possibility of very weak groups of higher energy neutrons. Evidence for such groups has been found by Cockcroft, Gilbert and Walton, although the activities reported were very small. The measurements do show, however, that $Q\leqq 0$ for the principal group of neutrons which agrees with the conclusions of Tuve and Hafstad.

THE ENERGY OF REACTION IN THE ACTIVATION OF OXYGEN

The angle of recoil of F^{17} was measured in order to check the estimate of the energy of activation of oxygen as obtained from its excitation curve. Because of the short half-life of F^{17}, this was a much more difficult experiment than the corresponding measurement on carbon. A piece of optical quartz was used as a target and the angle of incidence of the beam was reduced to less than 5°. It was necessary to check the decay of each section of the collector strip in order to eliminate activities due to silicon and to carbon contamination; only three sections could be measured in the available time.

The angular distribution so obtained is shown as a histogram in Fig. 5. This may be interpreted only by comparison with the corresponding distribution from carbon. Enough activity was found between 45° and 180° to account for a background of about the same intensity as that found in the carbon distribution; this background is shown as a dotted line in Fig. 5. If the back-

[11] Unpublished.

[12] Neddermeyer and Anderson, Phys. Rev. **45**, 653 (1934); Alichanow, Alichanian and Dzelepow, Nature **133**, 950 (1934); Cockcroft, Gilbert and Walton, cf. 7.

[13] Tuve and Hafstad, Phys. Rev. **48**, 106 (1935).

ground is subtracted from the curve, only a small activity remains in the region 30°–45°; this activity is of about the same intensity as that previously ascribed to scattering and it is probably due to the same cause. In short, the distribution found for oxygen would be nearly the same as that for carbon if the carbon curve were shifted about 15° toward smaller angles. The maximum angle of projection may, then, be taken as approximately 30° and from Eq. (6) $Q=-1.3$ MV. The agreement with the value $Q=-1.8$ MV as obtained with the excitation curve is as good as could be expected in an experiment of such low resolving power.

In conclusion, the author wishes to express his thanks to Professor Lawrence and to other workers in the laboratory for their assistance and advice in this work. The financial support of the Research Corporation and the Chemical Foundation is gratefully acknowledged.

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Rotational Structure of the Schumann-Runge Bands of Oxygen in the Vacuum Region

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Absorption bands of the Schumann-Runge system of oxygen have been photographed with a 3-meter vacuum spectrograph in the region λ1760−λ1925. A rotational analysis yields constants for the upper states which are new in the range $v'=8$ to 15 inclusive. Origins of the bands in this progression are represented within the limits of accuracy of the observations by the following equation:

$$\nu_{(v',\,0)}=49{,}014.93+700.360(v+\tfrac{1}{2})-8.0023(v+\tfrac{1}{2})^2-0.37535(v+\tfrac{1}{2})^3.$$

The energy of dissociation, D_0'', is 5.05 volts.

INTRODUCTION

A ROTATIONAL analysis of absorption bands of the Schumann-Runge system of O_2 obtainable in air at atmospheric pressure has been made by Curry and Herzberg,[1] who obtained data on the upper vibrational levels $v'=1$ to 7 inclusive. In the course of some experiments on absorption in the vacuum region of diatomic gases at low pressures, we obtained clearly resolved rotational structure of further members of the system, and have been able to extend the analysis to $v'=15$. The emission bands of this system all lie on the long wave-length side of the origin of the system and involve no upper levels with v' greater than 2; hence the absorption bands furnish the only available information about the higher levels of the upper electronic state, and we are reporting briefly the results of our analysis.

EXPERIMENTAL

The spectrograph used was designed by Professor H. E. White and built in the shops of the Physics Department. The design is similar to that of the 2-meter instrument described by Jeppesen,[2] except for the enlarged dimensions required to accommodate the 3-meter grating. The grating was ruled with about 14,000 lines per inch, at the National Physical Laboratory, in England. Light from the slit falls on the grating at a grazing angle of about 7 degrees, and the plateholder covers the range 0–3100A in the first order. Two oil diffusion pumps in series, backed by a Megavac pump, exhaust the 180-liter receiver to 10^{-5} mm in about one hour. During the absorption experiments, tank oxygen was admitted directly to the receiver at pressures ranging from 0.02 to 20 mm. At higher pressures in the receiver, the flow of gas through the slit to the discharge tube was too rapid to be balanced

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* Now at Ohio State University.
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[1] Curry and Herzberg, Ann. d. Physik **19**, 800 (1934).
[2] C. R. Jeppesen, Phys. Rev. **44**, 165 (1933).

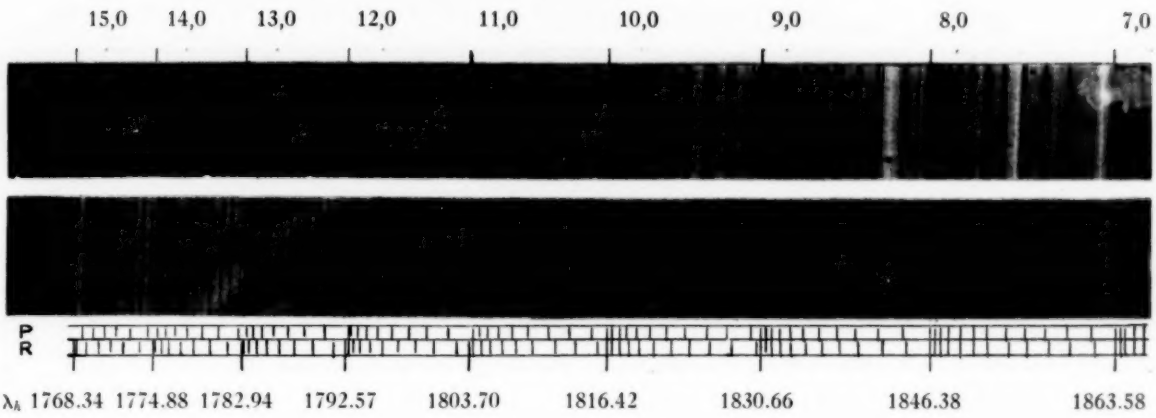

FIG. 1. Absorption bands of the Schumann-Runge system of O_2, showing rotational structure. Absorption lines are black in the reproduction. Pressure of O_2 in receiver, upper strip 15 mm, lower strip, 5 mm.

by the pumping system attached to the latter.

The source of light was a condenser discharge through a glass capillary tube, the arrangement being patterned after that of Rathenau.[3] The capillary, 30 cm long and 1 mm in inside diameter, was sealed on the end of a tapered glass tube which had a ground surface fitting into the tubular grounded electrode, and another ground surface into which the high potential electrode support was placed. Both electrodes were water cooled, so that stopcock grease could be used for assembling the tube. The capillary had to be replaced after each exposure because the interior was eroded to double the diameter by the discharge. The condenser had a capacity of 2 mf and it was charged by means of a transformer and two kenotrons to the voltage at which the discharge occurred through the capillary. It was found advisable to have a protective gap in parallel with the discharge tube to avoid shattering the glass by excessive voltages built up when the pressure in the tube became too low to conduct the discharge. The parallel gap was set to break down at about 20,000 volts, and the tube was pumped so as to operate at slightly less than that voltage. An exposure of 15 minutes comprising about 2000 sparks was required to produce strong blackening of the plates.

Wave-lengths were determined with the aid of a graph of deviations from linear dispersion prepared for each plate. A few emission lines as well as absorption lines appeared on our plates, but not enough were present to provide satisfactory standards. On one of our plates emission bands of the fourth-positive system of CO were present together with the Schumann-Runge absorption bands, the former having appeared during a prolonged warming up of the capillary by means of an ordinary 60-cycle high voltage transformer discharge. The wave-lengths of the CO heads as given by Read[4] served to establish a correction curve for the plate which was used to obtain satisfactory values for selected Schumann-Runge band lines on the same plate. The latter, in turn, were then available for plotting the corrections on other plates on which direct standards were lacking. A few of the lines recently remeasured by Boyce and Rieke[5] appeared on some of the plates, and indicated that the absolute error probably is less than 0.05A. The relative error in any band appears to be less than 0.02A. Lines 0.12A apart were clearly resolved.

RESULTS

The bands reproduced in Fig. 1 illustrate the extent of the resolution of the band structure. In bands near the origin of the system, the lines $P(K)$ and $R(K+2)$ are closer together, and cannot be resolved near the heads of the bands. Observed lines as assigned are listed in Table I, the letter P or R being used to call attention to a line which is assigned in both branches. No Q branch is expected or observed in these bands.

[3] G. Rathenau, Zeits. f. Physik **87**, 32 (1933).

[4] D. N. Read, Phys. Rev. **46**, 571 (1934).

[5] Boyce and Rieke, Phys. Rev. **47**, 653 (1935).

TABLE I. *Observed band lines, in cm* $^{-1}$.

K	$R(K)$	$P(K)$
	(4,0) ν_0 = 51,969.6	
1		51,972.3 R
3	51,972.3 P	960.7 R
5	960.7 P	945.9 R
7	945.9 P	922.7 R
9	922.7 P	900. R
11	900. P	868. R
13	868. P	830. R
15	830. P	
	(5,0) ν_0 = 52,562.6	
1		52,560.2 R
3	52,560.2 P	550.0 R
5	550.0 P	534.5 R
7	534.5 P	513.8 R
9	513.8 P	487.4 R
11	487.4 P	454.9 R
13	454.9 P	417.5 R
15	417.5 P	374.1 R
17	374.1 P	325.3 R
19	325.3 P	271.2 R
21	271.2 P	211.1 R
23	211.1 P	
	(6,0) ν_0 = 53,124.3	
1	53,125.4	53,122.0 R
3	122.0 P	111.5 R
5	111.5 P	095.7 R
7	095.7 P	074.1 R
9	074.1 P	046.5 R
11	046.5 P	53,013.3 R
13	53,013.3 P	52,974.5 R
15	52,974.5 P	930.2 R
17	930.2 P	879.6 R
19	879.6 P	823.7 R
21	823.7 P	762.1 R
23	762.1 P	694.3 R
25	694.3 P	620.5 R
27	620.5 P	

K	$R(K)$	$P(K)$
	(7,0) ν_0 = 53,658.5	
1	53,660.1	53,656.1 R
3	656.1 P	645.2 R
5	645.2 P	629.8 R
7	628.8 P	606.9 R
9	606.9 P	579.1 R
11	579.1 P	545.0 R
13	545.0 P	506.8
15	504.0	461.1
17	457.1	408.6
19	405.2	351.1
21	348.0	287.9
23	283.9	218.4
25	213.6	142.3
	(8,0) ν_0 = 54,158.9	
1	54,160.0	54,154.7 R
3	154.7 P	146.2
5	143.0	130.7
7	126.6	107.3
9	102.0	079.2
11	073.5	044.1
13	54,037.7	54,003.2
15	53,997.7	53,956.3
17	950.2	903.1
19	895.5	844.5
21	836.9	779.3
23	770.6	707.7
25	699.0	
	(9,0) ν_0 = 54,624.4	
1	54,625.1	54,619.4 R
3	619.4 P	610.5
5	607.5	594.1
7	590.2	571.2
9	565.8	541.7
11	536.3	506.0
13	499.5	464.8
15	456.1	416.4
17	407.3	362.0
19	351.7	301.2
21	289.7	233.7
23	221.7	

K	$R(K)$	$P(K)$
	(10,0) ν_0 = 55,053.3	
1	55,053.4	55,048.5 R
3	048.5 P	55,040.3
5	036.1	55,021.5
7	55,017.3	54,998.2
9	54,992.2	968.6
11	960.5	932.1
13	922.7	889.0
15	878.1	839.3
17	826.6	782.8
19	769.9	720.5
21	704.3	649.8
23	632.9	
	(11,0) ν_0 = 55,441.5	
1	55,441.6	55,436.4 R
3	436.4 P	428.1
5	423.2	409.9
7	403.8	385.7
9	377.4	355.4
11	344.3	316.5
13	304.5	271.3
15	257.8	220.9
17	204.1	163.3
19	144.1	097.6
21	076.7	
	(12,0) ν_0 = 55,786.9	
1	55,785.8	55,780.5 R
3	780.5 P	773.1
5	767.5	754.7
7	746.6	729.6
9	719.0	697.6
11	684.2	658.8
13	642.7	612.4
15	593.6	559.0
17	537.3	499.4
19	474.8	—

K	$R(K)$	$P(K)$
	(13,0) ν_0 = 56,087.6	
1	56,086.5	—
3	080.2	56,073.3
5	066.1	055.1
7	044.7	56,029.0
9	56,015.5	55,996.1
11	55,979.5	955.3
13	935.6	907.5
15	884.7	852.2
17	825.7	—
	(14,0) ν_0 = 56,342.6	
1	56,341.9	—
3	334.9	56,327.6
5	320.0	308.9
7	297.*	282.2
9	266.4	247.4
11	228.1	206.7
13	183.6	155.5
15	128.1	099.1
	(15,0) ν_0 = 56,551.0	
1	56,550.2	
3	542.9	56,534.9
5	527.5	519.5*
		515.4*
7	505.2	494.0
	501.6	483.8
9	471.6	457.9
	468.1	451.9
11	431.8	412.4
	427.7	407.6
13	383.8	360.3
	378.7	355.2

* blend
P, R indicate lines assigned in both branches.

Both the upper and the lower electronic states are triplets, but the triplet separation is too small to be observed in these bands, as is clearly seen in Fig. 1. However, in the (14,0) band, the lines are slightly broadened, and in the (15,0) band they are clearly doubled. This splitting is much greater than that found in the emission bands as discussed by Lochte-Holtgreven and Dieke,[6] which appears with higher K values. In the (16,0) band, the structure is too complicated to be followed. No explanation is offered for these observed perturbations.

The rotational constants of the upper states have been deduced from the data of Table I by the following method, in order to avoid emphasis on values displaced by blending of lines. Making use of the relationship:

$$R(K)-P(K)=\Delta_2F'(K)$$
$$=4B'(K+\tfrac{1}{2})-8D'(K+\tfrac{1}{2})^3$$

the values of $\Delta_2F'(K)/(K+\frac{1}{2})$ were plotted against $(K+\frac{1}{2})^2$, and the best straight line was drawn through the points for each band. The intercept at $K=-\frac{1}{2}$ is $4B'$. The values of B' are expressible as a function of v' by the following equation, of which the coefficients were obtained by the method of least squares:[7]

$$B'=0.801-0.00651v'$$
$$-0.001079v'^2-0.0000056v'^3.$$

The calculated values are listed in Table II. Also listed are the constants for the lower state, based on the work of Mecke and Baumann[8] on the atmospheric absorption bands in which the frequency resolution is much greater than here.

The origin of each band was computed with the smoothed (calculated) values of B', and the B'' values just mentioned, for four selected lines

[6] Lochte-Holtgreven and Dieke, Ann. d. Physik **3**, 937 (1929).

[7] Use was made of the abbreviated method of computing devised by Birge and Shea, U. Calif. Pub. Math. **2**, 67 (1927).

[8] Mecke and Baumann, Zeits. f. Physik **73**, 139 (1931).

TABLE II. *Rotational constants.*

v'	B'_v calc. (cm^{-1})	Obs.-Calc. (cm^{-1})
0	0.801	—
1	0.793	+0.005*
2	0.784	+ 1*
3	0.772	− 2*
4	0.757	− 3*
5	0.741	− 6*
6	0.722	− 3
7	0.701	+ 2
8	0.677	− 6
9	0.651	± 0
10	0.622	+ 11
11	0.591	+ 2
12	0.558	− 4
13	0.522	+ 1
14	0.483	+ 9
15	0.442	− 11

* Observed values from Curry and Herzberg,[1] also the following data: $D'=4.38\times10^{-6}$ cm^{-1}; $B''=1.4377$ cm^{-1} and $D''=4.88\times10^{-6}$ cm^{-1}.

TABLE III. *Origins of absorption bands.*

v', v''	νcalc. (cm^{-1})	Obs.-Calc. (cm^{-1})
0,0	49,363.1	—
1,0	50,046.2	−0.6*
2,0	50,710.0	+0.7*
3,0	51,352.4	−0.2*
4,0	51,970.3	−0.7
5,0	52,562.4	+0.2
6,0	53,126.1	−1.8
7,0	53,659.2	−0.7
8,0	54,159.3	−0.4
9,0	54,624.3	+0.1
10,0	55,051.9	+1.4
11,0	55,439.9	+1.6
12,0	55,786.0	+0.9
13,0	56,087.9	−0.3
14,0	56,343.4	−0.8
15,0	56,550.2	+0.8

* Observed values from Curry and Herzberg.[1]

in each band. The origins are represented with adequate accuracy by the equation[7]

$$\nu_{(v',\,0)}=49{,}014.93+700.360(v+\tfrac{1}{2})-8.0023(v+\tfrac{1}{2})^2-0.37535(v+\tfrac{1}{2})^3.$$

In Table III the computed values are listed, together with residuals (obs.-calc.) based on Curry and Herzberg's values for $v'=1$ to 3 and our values for the other origins. The extrapolated value for the origin of the (0,0) band is 49,363.1 cm^{-1}, which is 5.4 cm^{-1} greater than that obtained by the extrapolation of Curry and Herzberg.

DISCUSSION

On the basis of data available in 1929, Birge[9] found it necessary to use two parabolas to represent ω_v as a function of v for the "B" level of oxygen, whereas the present data are adequately represented by a single parabola. The earlier data were taken from the work of Leifson[10] and some unpublished work of Pulskamp.[11] In neither case was the fine structure completely resolved; in fact, Leifson observed only band heads. This lack of resolution, together with the scarcity of suitable standards, is quite enough to account for the complications encountered by Birge. The present data extend to an energy of vibration representing 96 percent of that required for dissociation. Extrapolation leads to a value of 7.01 electron volts, compared with 7.05 electron volts based on the earlier data. Assuming that the molecule dissociates from this state into one unexcited atom, and one ^1D atom with 1.96 electron volts energy, the value obtained for D_0'' is 5.05 electron volts.

[9] R. T. Birge, Trans. Faraday Soc. **25**, 707 (1929).
[10] S. W. Leifson, Astrophys. J. **63**, 73 (1926).
[11] C. A. Pulskamp, Ph.D. Thesis, U. of California (1929).

ACKNOWLEDGMENTS

The authors have enjoyed discussions with Professor F. A. Jenkins throughout this work, and have been materially aided by his generous assistance. They acknowledge with thanks also the interest of Professor R. T. Birge in the analysis. The senior author is particularly thankful for the excellent research facilities provided for him by the Department of Physics at Berkeley during his vacation from the Ohio State University.

A New Afterglow Spectrum in Nitrogen

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A new nitrogen afterglow spectrum is described in which the Vegard-Kaplan bands, which are emitted by the $A^3\Sigma$ metastable molecule, are the most intense components. This afterglow is associated with very weak discharges in tubes which are in a condition to give the auroral afterglow at higher currents. Attention is called to the fact that each of the three distinct nitrogen afterglow spectra is associated with a characteristic discharge spectrum.

ABOUT the start of the present century the late Professor Lewis of Berkeley discovered the first nitrogen afterglow.[1] This afterglow led to considerable study during the past thirty years, and to the discovery of many new spectra of gases that were added to the nitrogen. The strongest radiation in the afterglow is in the green, yellow and red, and it consists of selected members of the first-positive system of nitrogen. There are also some infrared bands belonging to the first-positive system in the afterglow, but these are very weak and of no great importance. Many attempts have been made to explain the afterglow, and in 1928 Cario and I[2] proposed an explanation in terms of metastable molecules of nitrogen and metastable atoms. This explanation seemed to account well for the phenomenon although I felt very soon after its publication that with further discoveries it would have to be revised. Such revision has been proposed by Okubo and Hamada,[3] and further revision is bound to develop from the present series of experiments.

The chance observation in 1928 that the addition of a trace of oxygen resulted in the excitation in the afterglow of the aurora green line 5577.35[4] raised in my mind the idea that the auroral spectrum and active nitrogen had a great deal in common. In spite of the apparently conclusive nature of that experiment I was certain that much more had to be done before a really aurora-like excitation of the green line could be achieved in the laboratory. The strong beta-bands of nitric oxide which are very strong on my 1928 plates are completely missing in both auroral and night sky spectra, in both of which the green line is so strong. Thus, my dissatisfaction with the excitation of the green line in active nitrogen was well founded.

The next significant step in this work came nearly three years after my first experiments, when in 1931[5] I discovered a new afterglow in nitrogen. It may be recalled that condensed discharges in nitrogen at fairly high pressures, or electrodeless ring discharges at low pressures, were required for the production of the Lewis-Rayleigh glow. I found it possible to produce strong afterglows in nitrogen with the use of uncondensed discharges at practically any pressures at which the gas would carry the discharge. The spectrum of this afterglow is now no longer completely made up of the first-positive bands. The first-negative bands of N_2^+, and some first-positive bands which originate on higher vibrational levels than those in the Lewis-Rayleigh glow, are now the strongest radiations in the visible, and the ultraviolet spectrum of the afterglow consists of the first-negative and the second-positive bands. In fact, the new afterglow was a practically perfect reproduction of the nitrogen radiations in the auroral spectrum, and this, with the addition of the strong green oxygen line and the two red oxygen lines, makes up practically the entire auroral spectrum. During the course of this work I discovered the so-called Vegard-Kaplan bands, the intercombination system corresponding to the transition $A^3\Sigma \rightarrow X^1\Sigma$.[6]

During the past year I have attempted to increase as much as possible the intensity of the Vegard-Kaplan system relative to the strong second-positive and first-negative systems. There

[1] E. P. Lewis, Ann. d. Physik **2**, 459 (1900); Phys. Rev. **18**, 125 (1904).
[2] Cario and Kaplan, Zeits. f. Physik **58**, 769 (1929).
[3] Okubo and Hamada, Phys. Rev. **42**, 795 (1932).
[4] Kaplan, Phys. Rev. **33**, 154 (1929).
[5] Kaplan, Phys. Rev. **37**, 1004 (1931); Phys. Rev. **45**, 671 (1934).
[6] Kaplan, Phys. Rev. **45**, 675 (1934).

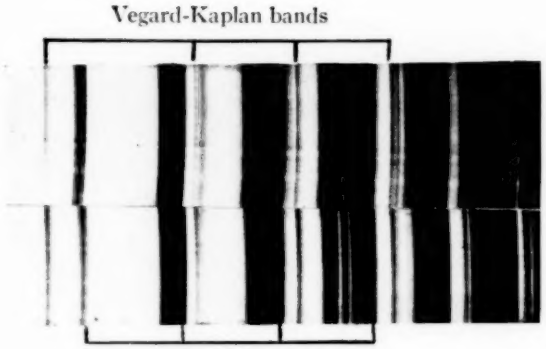

FIG. 1. Enhancement of Vegard-Kaplan bands relative to second-positive bands as current is diminished.

were several reasons for this investigation, the most important of which, to me at least, was the effort to identify convincingly the light of the night sky. This problem is to be presented in greater detail elsewhere. At first, I found that very rapidly interrupted discharges favored the Vegard-Kaplan system, and furthermore that the weaker the discharge the greater the relative intensity of these bands. Fig. 1 illustrates these results. It is to be noted that the new Goldstein-Kaplan bands are missing.

These very feeble discharges were accompained by a very weak blue afterglow to which I paid little attention until I began to suspect that perhaps the blue afterglow was but a weak visible sign of a strong ultraviolet glow. A 24-hour exposure on the afterglow showed the startling result that the Vegard-Kaplan bands were considerably stronger relative to the second positive bands than even in the best of the rapidly interrupted discharge spectra. A seven-day exposure yielded a plate strong enough to enlarge and to print, and this is shown in Fig. 2. It is to be noted that the first-negative bands are completely missing. The strong metastable molecular radiation in this nitrogen afterglow shows conclusively that they are the real parent substance in nitrogen afterglows, to use a radioactive expression. The present third nitrogen afterglow seems to be the most fundamental of the three so far discovered.

All of the above observations were made when the pressure in the tube was about 10^{-2} mm. Preliminary experiments show that the increase in the relative intensity of the Vegard-Kaplan system occurs at higher pressures also.

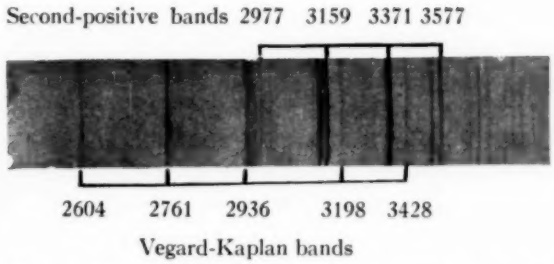

FIG. 2. New afterglow spectrum taken on Hilger E-31 spectrograph, showing enhancement of Vegard-Kaplan bands relative to second-positive bands.

Although no measurements of the tube currents have been made it is easy to describe the conditions under which these observations have been made. The tube is the same one in which the intercombination bands were discovered and the current was gradually diminished until a visible discharge barely managed to exist in the tube.

It should be pointed out that the three afterglow spectra of nitrogen are associated with electrical discharges each of which has a characteristic spectrum. Thus, the most striking property of the condensed discharge which produces the Lewis-Rayleigh afterglow is the presence in it of the fourth-positive bands of N_2. Associated with the discharge that is responsible for the second afterglow are the Vegard-Kaplan bands, the first-negative system of N_2^+ and first-positive bands that originate on very high vibrational levels. With the third afterglow we can associate a discharge in which the Vegard-Kaplan bands are relatively much more intense than with the second. The existence of these three discharge spectra suggests that the afterglows must be studied not only by means of their spectra but also with the discharge spectra in mind.

Although no mention was made of the Vegard-Kaplan bands in describing the second afterglow spectrum, it must be pointed out that they are present but with such small intensity that they serve only to prove that metastable molecules are present in this afterglow.[7] In fact, their presence, however weakly, in this second afterglow was cited as the first direct evidence for the existence of metastable nitrogen molecules in active nitrogen.

[7] Kaplan, Nature **134**, 289 (1934).

Remarks on the Redshift from Nebulae

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Some critical considerations are advanced, concerning the theory of the expansion of the universe. The main purpose of this paper is to indicate how a *statistical theory* can be developed which makes it possible to discuss in a very general way a number of features of the redshift of light through intergalactic space. In particular the problem of the width of spectral lines from distant nebulae is treated. Finally some observational tests are proposed which promise to throw new light on the problem of the redshift.

1. INTRODUCTION

IN recent years numerous attempts have been made to treat theoretically the problem of the redshift of light from extragalactic nebulae. Best known are the various theories which have sought to interpret this redshift on the basis of expanding models of the universe treated with the help of relativistic mechanics. Many other proposals, however, have been advanced. At the present time the relativistic theories are perhaps the only ones which derive their justification more or less directly from a set of equations whose validity is established to a high degree in other fields of physics and astronomy. In spite of this alluring feature the theory of the expanding universe can hardly be considered as a completely satisfactory solution of the problem of the redshift. Some of the following objections might be raised.

(a) The fundamental equations of the general theory of relativity are admittedly incomplete, inasmuch as they do not organically include the electromagnetic field and the phenomena related to the quantum of action. A *unified* field theory may well lead to conceptions about time and space which are fundamentally different from our present notions. For instance, the now abandoned theory of distant parallelism did not even allow of isotropy of space. The assumption of isotropy, however, constitutes an essential part of the current theory of the expanding universe.

(b) Even if we admit the validity of the equations of the ordinary theory of general relativity for limited regions of space and time, it is by no means certain whether these equations can be applied to the universe as a whole without taking into account retardation effects caused by the finiteness of the speed of light. Gravitation, according to the general theory of relativity, is a *cooperative phenomenon*,[1] inasmuch as all physical actions related to gravitation and inertia in a given point are not wholly determined by any limited regions which surround this point. The influence of even the most distant masses is indeed essential. In a universe, populated by moving masses, it is therefore not permissible to assume homogeneity without proving that the forces which are available in the universe are capable of maintaining homogeneity.[2] Stationary solutions of the gravitational equations of general relativity can give reliable results only in regions whose linear dimensions L are small, compared with a certain critical distance d, which is

$$d=cT, \tag{1}$$

where c denotes the velocity of light and T is equal to the average time in which are completed radical local rearrangements of the biggest individual stable agglomerations (systems) of matter. If we may identify these systems with the individual nebulae, then

$$T=\Lambda/\bar{v}, \tag{2}$$

where Λ is the "mean free path" of a nebula and $\bar{v}$ its average velocity. From observations on extragalactic nebulae[3] we know that approximately $\Lambda=10^6$ L.Y. (light years) and $\bar{v}=1000$ km/sec. The regions of space to which stationary solutions can safely be applied therefore have

[1] On the classification of cooperative phenomena see F. Zwicky, Phys. Rev. **43**, 270 (1933).

[2] See also R. C. Tolman, *Relativity, Thermodynamics & Cosmology* (Oxford, 1934), p. 483.

[3] F. Zwicky, Helv. Phys. Acta **6**, 110 (1933).

linear dimensions L which must satisfy the inequality

$$L \ll cT = 3 \times 10^8 \text{ L.Y.} \tag{3}$$

On all of the present cosmological theories the diameter D of the universe is

$$D > 2 \times 10^9 \text{ L.Y.} \tag{4}$$

The inequality (4) is also borne out by direct observations. The faintest nebulae which can be reached with the 100″-telescope are probably at distances of the order of 10^9 L.Y. All of the present relativistic stability considerations are based on stationary solutions of Einstein's equations and cannot be considered as conclusive.

Another serious difficulty is related to the fact, that in all of the recently advanced relativistic "models" of the universe use is made of notions, such as homogeneity, transfer of rigid meter sticks, etc., which have never been rigorously defined by actual physical operations.

(c) E. Hubble[4] has shown from his counts of nebulae, that a uniform distribution of these objects in a flat space is obtained if one corrects their apparent brightness for the loss of energy caused by the observed redshift. If, on the other hand, one assumes that the universe is expanding, the uniformity of the distribution of nebulae follows only if some additional assumption is introduced to compensate the effects of the general expansion, e.g., curvature of space, etc. As long as no further observations are available, it is therefore scientifically more economical *not* to link the redshift from nebulae with any *purely hypothetical* curvature and expansion of space.

(d) The dispersion of apparent velocities in clusters of nebulae constitutes a considerable part of the average apparent velocity of recession of these clusters. The coma cluster, for example, has a redshift of approximately 7000 km/sec. with a scattering of about 3000 km/sec. between its individual member nebulae. On the theory of the expanding universe no explanation has been advanced for this very important fact.

For the above reasons cautiousness requires not to interpret too dogmatically the observed redshifts as caused by an actual expansion. More experimental information is badly needed before we can hope to arrive at a satisfactory theory. The following lines contain an attempt to guide the theoretical and experimental researches on the subject in question in new directions.

2. Probability Considerations Related to the Redshift from Nebulae

We consider the following problem. A light quantum $h\nu_0$ is emitted from a nebula N located at a distance D from the observer O. Suppose that on the path NO there are n equidistant points or *stations*, which act as obstacles in such manner that the quantum $h\nu_0$, with a probability p, may lose an increment $h\delta$ at any station. For simplicity we assume that p and δ are independent of the frequency ν, inasmuch as we consider only small changes of ν_0. The probability for the quantum $h\nu_0$ to arrive at O with the reduced energy $h(\nu_0 - i\delta)$ is $I_i^{(n)}$, where

$$I_i^{(n)} = \binom{n}{i} p^i (1-p)^{n-i}. \tag{5}$$

We shall call $I_i^{(n)}$ the intensity factor of the frequency $\nu_0 - i\delta$. The relation (5) is obtained from the following obvious recurrency relation for the intensity factors

$$I_i^{(n)} = pI_{i-1}^{(n-1)} + (1-p)I_i^{(n-1)} \tag{6}$$

in conjunction with the theorem (7) for the binomial coefficients

$$\binom{n}{i} = \binom{n-1}{i-1} + \binom{n-1}{i}. \tag{7}$$

Monochromatic light of the frequency ν_0 from the nebula N therefore arrives at O as a spectrum of frequencies ν_0, $\nu_0 - \delta$, $\cdots$ $\nu_0 - i\delta$, $\cdots$ $\nu_0 - n\delta$, with the intensity factors $I_0^{(n)}$, $I_1^{(n)}$, $\cdots$ $I_i^{(n)}$, $\cdots$ $I_n^{(n)}$. As we have assumed that our quanta are not deflected from the straight path, all of them arrive at O, with more or less reduced energies, and the sum of the intensity factors must be

$$\sum_{i=1}^{n} I_i^{(n)} = 1. \tag{8}$$

This condition is satisfied, because

[4] E. Hubble, *The Halley Lecture* (Oxford, May, 1934).

$$\sum_i I_i^{(n)} = \sum_i \binom{n}{i} p^i (1-p)^{n-i}$$

$$= [(1-p)+p]^n = 1. \quad (9)$$

3. Values of the Intensity Factors for a Large Number of Stations

In discussing the spectral distribution of the intensity factors, two cases A and B must be distinguished.

Case A

Monochromatic light of frequency ν_0, emitted at N, arrives at O as a spectrum, whose maximum intensity is still at ν_0, or, $I_{i+1}^{(n)} < I_i^{(n)}$ and in particular $I_1^{(n)} < I_0^{(n)}$. The condition for this to be true is

$$np/(1-p) < 1. \quad (10)$$

I shall not discuss this case any further, as it does not correspond to a shift of the maximum of the spectral lines and therefore has little significance for the theory of the redshift from nebulae.

Case B

The maximum intensity of a spectral line is shifted to a lower frequency when light travels from N to O. This implies that at least $I_1^{(n)} > I_0^{(n)}$ or

$$np/(1-p) > 1. \quad (11)$$

Three simple subcases B_1, B_2 and B_3 may be distinguished, which we now proceed to analyze.

Subcase B_1. We assume that $p = 1$, independent of how many stations we choose on the path NO. We also put $\delta = \Delta/n$ where Δ is a function of D and ν only, but is independent of n.

The interpretation of redshift as caused by an expanding universe falls into this category. We evidently have

$$I_0 = I_1 = \cdots = I_{n-1} = 0 \qquad I_n = 1. \quad (12)$$

A spectral line on its way from N to O is shifted "bodily" from ν_0 to $\nu_0 - \Delta$. There is no widening of the line.

The remaining two cases deal with probabilities $p < 1$. For reasons which will become apparent later on, we are particularly interested to find the *displacement* and the *widening* of spectral lines for large values of n.

Subcase B_2. We assume, $p = \text{constant} < 1$, and simultaneously $\lim_{n=\infty} n = \infty$, $\lim_{n=\infty} \delta = 0$ in such a manner that always $n\delta = \Delta\nu(D)$. This means that at *every* station the incoming frequency can lose an increment δ. As we increase the number of stations n on a given path $NO = D$ the probability p for a change of frequency to take place at any individual station stays constant, but the magnitude of the change decreases. Every station has a real physical significance. In real physical problems n will of course never be infinitely large, so that our calculations for $n = \infty$ will give asymptotic representations of the actual phenomena.

The proposal which I made a few years ago,[5] that a "gravitational drag" on light is responsible for the redshift from nebulae, falls into this category B_2. A gravitational drag arises in this manner. We consider a stationary gravitational system, in our case the universe, which contains matter and radiation. Suppose that a given body C of this system suddenly divides into two parts C_1 and C_2. In our case C_1 is, for instance, a star and C_2 is a light quantum $h\nu$ which is emitted from it and which sooner or later is absorbed as a quantum $h\nu'$ by some other body C'. If now all of the bodies C, C', C'', $\cdots$, were immovable relative to one another, then according to the theory of relativity

$$(\nu - \nu')/\nu = (\Phi' - \Phi)/c^2, \quad (13)$$

where Φ and Φ' are the gravitational potentials on C and C', respectively. If, however, all the bodies are freely movable under their mutual gravitational actions, the rearrangement of matter caused by the transfer of the mass $h\nu/c^2$ from C to C' involves in general an additional loss of energy for the quantum $h\nu$. The magnitude of this loss is essentially determined by retardation effects which are not included in formula (13).

Mathematically, subcase B_2 is closely related to a problem of probabilities first treated by de Moivre. It is seen at once that the terminal intensity factors $I_0^{(n)} = (1-p)^n$ and $I_n^{(n)} = p^n$, for $n = \infty$ tend towards zero faster than $1/n$. The intensity factors therefore possess a maxi-

[5] F. Zwicky, Proc. Nat. Acad. Sci. **15**, 773 (1929); Phys. Rev. **34**, 1623 (1929).

mum I_i between I_0 and I_n at some index $i=\alpha n$. We proceed to determine α, assuming that n, αn and $n(1-\alpha)$ are simultaneously large numbers. We make use of Stirling's asymptotic formula for the factorials

$$\lg x!=(x+\tfrac{1}{2})\lg x-x+\tfrac{1}{2}\lg 2\pi+R(x), \quad (14)$$

where $R(x)<1/12x$. We shall neglect the term $R(x)$. In this approximation we obtain as characteristic for the maximum

$$\alpha=p-(1-2p)/2n. \quad (15)$$

We may neglect $(1-2p)/2n$ as compared with p and expand I, approximating it by a Gaussian error curve. Putting $i=pn+\xi$ we finally have

$$I_{pn+\xi}=e^{-\xi^2/2np(1-p)}/[2\pi np(1-p)]^{\frac{1}{2}}. \quad (16)$$

The sum, taken over all of the intensity factors is unity, as it should be.

$$\sum_i I_i^{(n)}=\int_{-\infty}^{+\infty} Id\xi=1. \quad (17)$$

From (16) we see that the maximum intensity factor has a value which is proportional to $n^{-\frac{1}{2}}$. At the same time the characteristic width of the "spectrum" of the intensity factors comprises the range of indices from $pn-\xi_c$ to $pn+\xi_c$, where $\xi_c\propto n^{\frac{1}{2}}$. The intensity factor is indeed reduced to the value $I_{\max}/e$ for

$$\xi_c=[2np(1-p)]^{\frac{1}{2}}. \quad (18)$$

Our initially monochromatic beam of frequency ν_0 arrives at O as a spectrum whose intensity maximum lies at the frequency $\nu_m=\nu_0-p\Delta\nu$ and whose characteristic width W is

$$W=2\xi_c\delta=[8p(1-p)/n]^{\frac{1}{2}}\Delta\nu, \quad (19)$$

whereas the shift S of the spectral line is

$$S=\nu_0-\nu_m=p\Delta\nu, \quad (20)$$

the ratio of width to shift is

$$W/S=[8(1-p)/np]^{\frac{1}{2}}\propto n^{-\frac{1}{2}}. \quad (21)$$

As the number of stations n on the path $D=NO$ increases, the ratio W/S decreases proportional to $n^{-\frac{1}{2}}$. Hence, for great distances D the sharpness of the initial spectral line is preserved.

If the redshift has a cause whose statistical interpretation is covered by our subcase B_2 no appreciable widening of the spectral line can be expected.

Subcase B_3. We have simultaneously $\lim_{n=\infty} n=\infty$, $\lim_{n=\infty} p=0$, in such a manner that always $np=P(D)$, where $P>1$. P depends only on D, but is independent of n. At the same time $\delta=$constant, independent of n. This case corresponds to a problem of probabilities first treated by Poisson. It embraces such interpretations of the redshift which postulate the presence in space of a definite average number of obstacles which are distributed at random over the n stations on the path D. Changes of the frequency, caused by "direct contact" of light with electrons and atoms, such as the Compton effect, Raman effect, etc., may be classified under subcase B_3.

The distribution of the intensity factors is immediately obtained from our previous result (16) by putting $np=P$. The maximum intensity factor I_i has the index $i=P$ which is independent of the number n of stations chosen. We have

$$I_{p+\xi}=e^{-\xi^2/2P(1-P/n)}/[2\pi P(1-P/n)]^{\frac{1}{2}} \quad (22)$$

or, for $n=\infty$ $\quad I_{p+\xi}=e^{-\xi^2/2P}/(2\pi P)^{\frac{1}{2}}$. (23)

This result is also obtained immediately by a direct derivation of the intensity factor I_i for $n=\infty$, namely,

$$\lim_{n=\infty} I_i=\lim_{n=\infty}\frac{n!}{i!(n-i)!}(P/n)^i(1-P/n)^{n-i}$$

$$=P^ie^{-P}/i!. \quad (24)$$

Putting $i=P+\xi$ and assuming that P is a fairly large number we have asymptotically the approximation (23) for the intensity factors. The shift of the spectral line in this case becomes

$$S=P\delta \quad (25)$$

and the width of the resulting line

$$W=2\xi_c\delta=2(2P)^{\frac{1}{2}}\delta. \quad (26)$$

The ratio of width to shift is

$$W/S=(8/P)^{\frac{1}{2}} \quad (27)$$

tends toward zero as D and P increase. For great distances again there results no widening of the spectral lines.

All of those interpretations of the redshift, which with sufficient accuracy can be described by our simple statistical schemes will therefore not be associated with any appreciable widening of the spectrum of light which travels over long distances. In actuality no widening of spectral lines from more and more distant nebulae has so far been observed.

4. Generalizations of the Statistical Theory of the Redshift

The theory which I have presented in this paper of course does not give more than the most elementary ground work for a statistical interpretation of the redshift. The following generalizations might be considered:

(1) The probability p depends on the frequency ν and on the index i of the station.

(2) The change δ of the frequency ν depends on ν and i.

(3) The change δ at a given station is not unambiguous. The possible changes δ_{i1}, δ_{i2}, $\cdots$ occur with the probabilities p_{i1}, p_{i2}, $\cdots$.

(4) Finally a three-dimensional system of stations, which are distributed over the entire space, must be considered in order to incorporate such interpretations of the redshift which involve scattering of light.

Professor H. Bateman at our Institute has been kind enough to take up some of these problems. An account of his researches will appear in this journal.

5. Concluding Remarks

From the above it becomes apparent that considerations concerning the *spectral spreading* of light traveling over long distances are not likely to provide any definitely distinguishing tests between various interpretations of the redshift, even if they are as radically different from one another as was assumed in the cases B_1, B_2 and B_3.

If one looks for other effects which will furnish more decisive clues about the correct theory of the redshift, a consideration of the *spatial spreading* or scattering of light immediately suggests itself. Qualitatively the following conclusions are obtained.

All of the proposals which seek to interpret the redshift as being caused by obscuring matter, such as electrons, atoms, etc., must be discarded. Redshifts which result from the Compton effect, the Raman effect, and so on, are associated with a scattering of light which would produce impossibly large washing out of nebular images which actually are not observed.

The expansion of the universe, on the other hand, calls for no changes of nebular images except such as are caused by purely geometrical conditions which determine the path of light. The images therefore are not washed out.

The theory of the gravitational drag occupies a middle position inasmuch as different light quanta from the same nebula go through almost but not exactly identical changes on their path from the nebula to the observer. An initially parallel beam of light, on this theory, will gradually open itself because of small angle scattering. Observational tests on this point will be important.

In conclusion I mention in a preliminary fashion one more possibility to gain new information about the redshift from nebulae. From Hubble's counts of nebulae it follows, that in our "immediate" neighborhood of about 50 million light years about one percent of all nebulae are members of giant clusters. The question suggests itself whether this ratio between cluster nebulae and field nebulae is independent of distance. The mode of formation and duration of clusters of nebulae must be closely associated to the physical history of the universe as a whole. Observations of the relative number of nebulae in clusters promise to provide important material for further theories. It will also be essential to find out if the dispersion of velocities among the member nebulae of cluster is a function of distance. The proposal to test a possible relation between distance and dispersion of velocities has been advanced by Mt. Wilson astronomers in their research program.

The Computation of Spectral Intensities for Hydrogen

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A new form, designed to facilitate computation, is given for the radial integral involved in the theoretical intensities for the atomic hydrogen spectrum. A comparison is made between several published sets of numerical computations, and some corrections are made, both algebraic and arithmetical. The purpose throughout is to give information useful to anyone using or extending the published computations.

THE difficulty in numerical evaluation of the theoretical intensities in the atomic hydrogen spectrum[1] arises from the integral containing the radial wave functions. Many of the published results have been derived from unnecessarily cumbersome expressions for this integral, and the extent of the numerical tables now in the literature has been set by the labor of computation involved. This paper presents a new form for the general value of the radial integral which is better suited for numerical computation than any now published. Some corrections of the literature are also made.

NOTATION

n, l, and n_r will have their usual significance as quantum numbers, with

$$n-l-1=n_r. \tag{1}$$

n and n_r will ordinarily refer to the higher level and n' and n_r' to the lower level in a spontaneous transition. For the azimuthal quantum number, however, l^* and l' will refer, respectively, to the higher and lower levels, and the unprimed l will uniformly denote the numerically greater of the two numbers l^* and l'; thus

$$2l=l^*+l'+1. \tag{2}$$

With this meaning for l, r is defined, for $n'-l\geqq 1$, by

$$r=n'-l-1\geqq 0. \tag{3}$$

The following abbreviations will also be used:

$$\begin{aligned} u&=(n-n')/(n+n');\\ v&=1-1/u^2=-4nn'/(n-n')^2;\\ w&=v/(v-1)=4nn'/(n+n')^2. \end{aligned} \tag{4}$$

If a is the radius of the first Bohr orbit in hydrogen, Ra will denote the radial integral defined and designated as $R_{n,l}^{n',l'}$ by Bethe,[1] and as $C_{n_r,l}^{n_r',l'}$ by Gordon.[2]

THE GENERAL EXPRESSION FOR R

The simplest expressions which have been found for the radial integral involve two terminating hypergeometric series, the numbers of whose terms are fixed by the numerical value of the final radial quantum number, n_r'. A result of this type is given by Gordon.[2] In making a series of numerical evaluations from such a general formula, one proceeds best not by making all numerical substitutions immediately, but by assigning a numerical value to n_r' only, and summing the hypergeometric series algebraically with all other quantum numbers left general. Formulae specialized in this way have been given by Kupper.[3] The following discussion indicates a means of obtaining others for higher values of n_r' with a minimum of computational labor, which is considerable at best. (If one is interested only in total line intensities, a formula by McLean[4] should be useful.)

The following identities, by using the relations (1) and (4), and $n_r'=n'-l$, are readily obtained from relations between contiguous hypergeometric functions.[5]

[1] The discussion by H. Bethe, *Handbuch der Physik*, second edition, Vol. 24, Part I, on pp. 441 to 445 and those preceding, is taken here as a point of departure. For intensities in the Dirac theory, see Saha and Banerji, Zeits. f. Physik **68**, 704 (1931).

[2] Gordon, Ann. d. Physik **2**, 1031 (1929).

[3] Kupper, Ann. d. Physik **86**, 511 (1928).

[4] McLean, Phil. Mag. **18**, 845 (1934).

[5] Gauss, *Circa Seriem Inf. 1+· etc.*, Werke **3**, 130 (Göttingen, 1866).

$$F(-n_r, -n_r'; 2l; v)-u^2F(-n_r-2, -n_r'; 2l; v)$$

$$=\frac{4nn'}{2l}\left[\frac{-1}{n-n'}F(-n_r, -n_r'+1; 2l+1; v)+\frac{1}{n+n'}F(-n_r-1, -n_r'+1; 2l+1; v)\right] \tag{5}$$

$$=\frac{4nn'}{2l(n+l)}\left[\frac{n'-l}{n-n'}F(-n_r, -n_r'+1; 2l+1; v)+\frac{n'+l}{n+n'}F(-n_r, -n_r'; 2l+1; v)\right]. \tag{6}$$

With the aid of these relations, Gordon's Eq. (28)[2] for R may be put in the following form, applying to the transition $n, l^*\rightarrow n', l'$ with $\Delta l=l'-l^*=\pm 1$, and with the notations (2), (3), and (4).

$$R=2^{l^*+l'+4}n^{l'+3}n'^{l^*+3}\frac{(n-n')^{n-n'-1}}{(n+n')^{n+n'+1}}\left[\frac{(n+l^*)!}{(n'+l')!(n-l^*-1)!(n'-l'-1)!}\right]^{\frac{1}{2}}P_{\pm}. \tag{7}$$

Here P_- and P_+ (the subscripts corresponding to the sign of Δl) are polynomials in n and n' defined by terminating hypergeometric series as follows:

$$2n'P_-=(-1)^r[(n-n')^{2r}(2l+r)!/(2l)!][(n+n')F(-r, -n+l+1; 2l+1; v)$$
$$-(n-n')F(-r, -n+l; 2l+1; v)]. \tag{8}$$

(If $n'=l$, then $P_-=1/2n'(n^2-n'^2)$.)

$$2nP_+=(-1)^r[(n-n')^{2r}(2l+r)!/(2l)!][(n+n')(n-l)F(-r, -n+l+1; 2l+1; v)$$
$$-(n-n')(n+l)F(-r, -n+l; 2l+1; v)]. \tag{9}$$

(7) is in form a direct generalization of the special cases given by Kupper.[3] The first bracket in the right member of (8) or (9) is the common denominator of the terms in the series, and just clears them of fractions. Since, in the last factor in the right member of (8) the initial terms of the two series combine to the value $2n'$, the whole expression contains $2n^r$ as a factor. If also, in the second part of the right member of (8), the expression $(n-n')^{2r}F(-r, -n+l; 2l+1; v)$ is replaced by its equivalent (by using a familiar identity) $(n+n')^{2r}F(-r, n+l+1; 2l+1; w)$ it becomes apparent that either part of the right member of (8) is transformed into the other part by changing the sign of the upper quantum number n (since v and w are thereby interchanged). The entire expression is therefore an even function of n and equal to twice the even terms in either part. Similarly the right member of (9) is an odd function of n and equal to twice the odd terms in the first part. It therefore contains the factor $2n$. Hence if we write

$$F''+F'=(-1)^r[(2l+r)!/(2l)!](n-n')^{2r}F(-r, -n+l+1; 2l+1; v), \tag{10}$$

in which the two parts of the polynomial, F'' and F', are, respectively, even and odd functions of n, we have

$$n'P_-=n'F''+nF' \tag{11}$$

$$nP_+=n(n'-l)F''+(n^2-n'l)F'$$
$$=(n^2-n'^2)F'+(r+1)(nF''+n'F'). \tag{12}$$

If $(F''+F')$ is transformed into a series in u^2, and l eliminated from it by (3), the result may be considered a function of r and expanded as follows:

$$F''(r)+F'(r)=\sum_{i=0}^{r}(-1)^iC_i^r\frac{(n+n'-r-2+i)!(n-n'+r)!}{(n+n'-r-2)!(n-n'+i)!}(n-n')^{2i}(n+n')^{2(r-i)}. \tag{13}$$

C_i^r is the coefficient of x^i in the binomial expansion of $(1+x)^r$. F'' and F' are respectively of degree $3r$

and $(3r-1)$ in n and n', as indicated in the next paragraph. P_- and P_+ are both of degree $3r$, and are both even functions of n. When r is assigned a numerical value, (13), (11), (12), and (7) (with l^* and l' expressed in terms of n' and r) lead directly to a pair of formulae of the type given by Kupper, through the evaluation of a single hypergeometric series, as against the four which Gordon's formula would seem to involve.

The summation, for a numerical value of r, of the series (13) in u^2 proceeds a bit more readily than when the series is in terms of v or w. A convenient procedure is to collect like powers of $(n-n')(n+n')$. Even for the general value of r the terms of the two highest degrees in n and n' can be collected without too much difficulty. The result is:

$$F''+F'=(2n')^r(n^2-n'^2)^r+(2n')^{r-1}(n^2-n'^2)^{r-1}\cdot\tfrac{1}{2}r[n^2(r+5)+3n'^2(r+1)-4nn'] \\ +\text{terms of lower degree in } n \text{ and } n', \text{ the lowest being } 2r.$$

This gives: $P_-=(2n')^r(n^2-n'^2)^r+(2n')^{r-1}(n^2-n'^2)^{r-1}\cdot\tfrac{1}{2}r(r+1)(n^2+3n'^2)+\text{terms of lower degree.}$

$$P_+=(2n')^r(n^2-n'^2)^r+\text{terms of lower degree.}$$

It is also possible, of course, to express $[F''(r)+F'(r)]$ in terms of $F''(r-1)$ and $F'(r-1)$, but the relation does not seem to offer any advantage in simplicity over (13).

Specialized Formulae

Kupper[3] has given formulae for matrix amplitude squares, equal to $\frac{1}{2}lR^2$ in the present notation, for the cases $r\leqq 2$. An additional pair of formulae of the same type can be derived from the following values of P_- and P_+ for $r=3$.

$$\begin{aligned} P_-= \quad & 2n^6 \ (\quad 4n'^3 \ +12n'^2 \ + \ 19n' \ + \ 15) \\ & +2n^4n'^2(-12n'^3 \ +12n'^2 \ + \ 31n' \ + \ 27) \\ & +6n^2n'^4(\quad 4n'^3 \ -20n'^2 \ + \ 19n' \ + \ 15) \\ & +2n'^6 \ (- \ 4n'^3 \ +36n'^2 \ -107n' \ +105) \end{aligned} \tag{14}$$

$$\begin{aligned} P_+= \quad & 4n^6 \ (\quad 2n'^3 \ +21n'^2 \ +101n' \ +210) \\ & + \ 4n^4n'^2(- \ 6n'^3 \ -27n'^2 \ - \ 31n' \ + \ 90) \\ & +12n^2n'^4(\quad 2n'^3 \ - \ 3n'^2 \ - \ 11n' \ + \ 18) \\ & + \ 4n'^6 \ (- \ 2n'^3 \ +15n'^2 \ - \ 37n' \ + \ 30). \end{aligned} \tag{15}$$

All of Kupper's formulae have been rechecked and certain ones found in error. These will be referred to by the numeration of his paper.[3] There are obvious typographical errors in (47) and (51). (49), for the transition $4p-ns$, should read

$$2^{21}n^9(n-4)^{2n-10}(57n^4-608n^2+1280)^2/3\cdot 5(n+4)^{2n+10}$$

(52), for $5s-np$, should be by (14)

$$2^75^9n^7(n^2-1)(n-5)^{2n-12}(91n^6-2545n^4+20625n^2-46875)^2/3^2(n+5)^{2n+12}$$

and (57), for $5p-ns$, by (15),

$$2^{10}5^7n^9(n-5)^{2n-12}(149n^6-3725n^4+25875n^2-46875)^2/3^3(n+5)^{2n+12}.$$

The first of the above corrections has been made by Maxwell[6] but is repeated here for completeness.

[6] Maxwell, Phys. Rev. **38**, 1664 (1931).

Numerical Tables

Tables published by Slack,[7] Kupper,[3] Maxwell,[6] and Bethe[1] have been intercompared and largely recomputed with a view to eliminating numerical errors as completely as possible. Bethe's tables are the most recent, and are substantially correct, but are not as extensive as some of the others, which have accordingly been included in the following discussion.

The radial integral

Table I gives values of $\frac{1}{2}lR^2$ which should replace those in Kupper's tables[3] derived from the three incorrect formulae mentioned above. Table III contains further scattered corrections. Subject to this revision, Kupper's tables are correct, for $n \leqq 8$ when $n' \leqq 3$ and for $n \leqq 7$ when $n' > 3$, almost everywhere to one percent and everywhere to three percent. For higher values of n, inspection indicates occasional errors of five to ten percent and one of 50 percent. An extension to the transition 7→6 is given in Table II.

Bethe's Tables 15 and 16, pages 442 and 443,[1] subject to the minor corrections in Table III, are correct to within three percent, or to the last significant figure given, for $n \leqq 8$. The figures for the higher discreet and the continuous levels have not been examined.

Table I. *Amplitude squares, $\frac{1}{2}lR^2$, from corrected formulae, to be substituted in Kupper's tables.*[3]

n \ Transition	$4p-ns$	$5s-np$	$5p-ns$
5	10.6		
6	1.60	74.6	27.4
7	0.545	11.9	4.02
8	.258	4.14	1.34
9	.145	1.99	0.626
10	.0910	1.14	.351
11	.0615	0.721	.219
12	.0437	.490	.147

Table II. *Amplitude squares, $\frac{1}{2}lR^2$, supplementing Kupper's tables.*[3]

l \ Transition	$7, l \to 6, l-1$	$7, l-1 \to 6, l$
1	137.	59.05
2	398.	70.6
3	848.	58.9
4	1582.	36.3
5	2734.	14.1
6	4497.	

[7] Slack, Phys. Rev. **31**, 527 (1928).

Transition probabilities and intensities

Table IV contains the only corrections of more than a few percent to be made in Bethe's Table 17, page 444,[1] and extends that table to give transition probabilities and mean lives for the seventh state. Table V similarly corrects Bethe's Table 18a, page 445,[1] giving intensities. It should perhaps be mentioned that these intensities are energy radiated from *all* magnetic substates

Table III. *Corrections to tables.*

Transition	Values of $\frac{1}{2}lR^2$ to replace those of Kupper[3]	Values of R^2 to replace those in Bethe's Tab. 15[1]	Values of Bethe's $f_{nn'}$ to replace those in his Tab. 16[1]
$2p-6d$		0.438	0.022
$4s-7p$		4.25	
$4p-6s$		3.20	
$4p-7s$		1.09	.005
$4p-8s$		0.515	
$4p-6d$	19.2		
$4p-7d$		6.69	
$4d-6p$	1.26		
$4d-7p$		0.405	
$4f-5d$	4.14		
$4f-7d$		.094	.0006
$5p-6d$	230.		
$5d-6p$	29.5		
$5g-6h$	1852.		

Table IV. *Transition probabilities (units of 10^8 sec.$^{-1}$) and mean lives of excited states (units of 10^{-8} sec.), correcting and supplementing Bethe's Table 17.*[1]

Transition	n	1	2	3	4	5	6	Sum	Mean life
$6s \to np$						.0027			
$6p$ ns						.0024			
$6d$ np			.051			.0045			
$7s$ np			.0046	.0031	.0022	.0016	.0013	.0128	78.
$7p$ ns		.123	.0191	.0060	.0028	.0016	.0010		
nd				.0005	.0005	.0005	.0005	.1555	6.4
$7d$ np			.0311	.0115	.0053	.0029	.0017		
nf					.0001	.0002	.0003	.0531	18.8
$7f$ nd				.0123	.0073	.0043	.0026		
ng						.00005	.0001	.0266	37.6
$7g$ nf					.0064	.0055	.0037		
nh							.00003	.0156	64.
$7h$ ng						.0050	.0053	.0103	97.
$7i$ nh							.0074	.0074	135.
7 mean		.0075	.0044	.0034	.0031	.0032	.0045	.0261	38.3

TABLE V. *Corrections to Bethe's Table 18a[1] giving intensities in units of 10^{-4} erg/sec.*

Transition	$2p-6d$	$3p-5s$	$3p-7s$	$3p-8s$	$3d-8f$
Intensity	1.22	0.014	0.006	0.004	0.108

divided by the number of excited atoms in *each*, that is to say, radiation per $(2l^*+1)$ atoms.

Some errors remain in Slack's original[7] and revised[6] tables. These may be located by comparison with Bethe's Table 17 or Table IV, for $n \leqq 7$. Beyond this, Slack's values for $1s-8p$, $3d-9f$, $3p-9d$, $3p-9s$, and $2p-9d$, are, respectively, 26 percent, 8 percent, 15 percent, and about 10 percent high, and 5 percent low. Maxwell's table[6] for mean lives in ionized helium is also not entirely correct, and should likewise be compared with Bethe or Table IV.

I am indebted to Dr. F. G. Slack for much information and assistance received in our conversations. I also wish to acknowledge the assistance of Mr. W. J. Boyd, employed by the Federal Emergency Relief Administration, in making computations.

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The Energy Distribution of Electrons in the Photoelectric Effect

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The character of the photoelectric emission from a metal depends on the distribution of electron levels, the transition probabilities from these levels and the extent to which the levels are populated by electrons. The last of these is given by the Fermi factor. Various expressions have been suggested for the first two. These are discussed, and equations for the energy distribution derived in each case. The results are compared with experimental data for molybdenum, published by Roehr. In all cases the proportion of low energy electrons predicted appears to be too high. The theory of Mitchell comes nearest to fitting the experimental data over the low energy range. The stopping potential currents for higher energy, when plotted on a logarithmic scale as done by Roehr, fall nicely on the curve calculated on the theory of Mitchell. It is pointed out that the agreement obtained with such logarithmic plots is essentially a check on the dominating Fermi factor, and that the region of low energies in the energy distribution, for which the Fermi factor is practically unity, is the important one for studies of the electronic structure of metals.

INTRODUCTION

IN most theoretical treatments of electrons in metals[1] the state of the electrons is considered to be built up of a combination of single electron states, one for each electron, each state being characterized by a set of quantum numbers k and associated with a definite energy value ϵ. In theories of the photoelectric effect this view is always adopted, and it is furthermore assumed that each individual photoelectric process involves one single electron, originally of energy ϵ in the metal: as a result of the process this electron appears outside with an energy $u=\epsilon+h\nu$.[2]

[1] Cf. Slater, Rev. Mod. Phys. **6**, 209 (1934).

[2] Except in some theories for the selective effect, in which a process similar to an Auger effect is considered: Wolff, Zeits. f. Physik **52**, 158 (1929); Suhrmann, Ergebn. d. exakt. Naturwiss. **13**, 191 (1934); Zener, Phys. Rev. **47**, 15 (1935).

Under these conditions the energy distribution of the photoelectric emission produced by radiation of frequency ν can always be written.

$$f(u)du = F(\epsilon) \sum_{\epsilon,\, d\epsilon} P_k \tag{1}$$

with

$$F(\epsilon) = 1/(e^{(\epsilon-\epsilon_0)/kT}+1). \tag{2}$$

$F(\epsilon)$ is the Fermi factor, which gives the probability of finding an electron in a state of energy ϵ, when the temperature is T; ϵ_0 is the highest occupied energy state at $T=0$. P_k is the probability of emission from the state k, if occupied by an electron, and the summation is to be extended over all states of energy between ϵ and $\epsilon+d\epsilon$, the relation of ϵ to u being that stated above. In general P_k is a function of both ν and k. With a stopping potential V applied to the

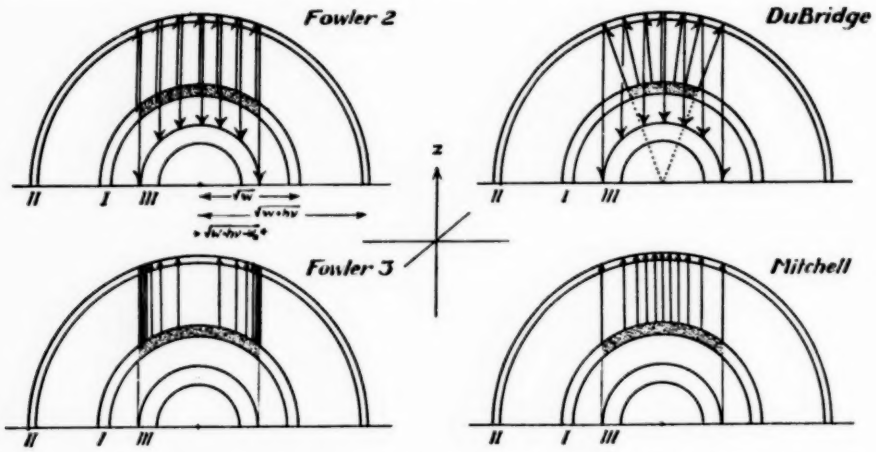

FIG. 1. Illustrating in momentum space the transitions occurring in the photoelectric effect, according to some of the hypotheses proposed. The density of transition lines indicates relative transition probability.

outer electrode in the usual spherical condenser arrangement—$(r/R)^2 \ll 1$—for determining the energy distribution, the current is of course given by

$$I(V) = e\int_{eV}^{\infty} f(u)du. \tag{3}$$

In principle both P_k and the distribution of electron states with respect to energy are uniquely determined, once the model of the metal has been chosen. Actually several different expressions for the saturation current ($V=0$) have been suggested, presumably all based on the Sommerfeld model of electrons in metals. This is due to the fact that whereas the function adopted to represent the distribution of electron states was correctly based on this model, an independent assumption was made about the form of P_k in some of the cases. This assumption was therefore not necessarily compatible with the model originally adopted.

In the following we shall consider the various hypotheses proposed for the transition probabilities in the Sommerfeld free electron model and compare the results to which they lead as regards the form of $f(u)$ and $I(V)$ with available experimental data.

THEORETICAL EXPRESSIONS FOR THE ENERGY DISTRIBUTION

According to the Sommerfeld model[3] the electron states can be represented by a distribution of points of constant density filling a three-dimensional momentum space, the Cartesian coordinates of which are proportional to the first three quantum numbers k. The fourth number stands for the spin. The number of states between ϵ and $\epsilon+d\epsilon$ is thus proportional to the volume of the spherical shell I in Fig. 1, of radii $w^{\frac{1}{2}}$ and $(w+dw)^{\frac{1}{2}}$—in units $(2m)^{\frac{1}{2}}$—where $w=\epsilon+w_a$ is the kinetic energy inside the metal, $-w_a$ being the potential energy of an electron in the interior of the metal. The direction of the normal to the metal surface will be taken to be that of the vertical z axis in this figure; only the upper half of the space with positive momentum components directed outwards is shown. For the purpose of illustration we may say, that an electron in one of the states I upon absorption of light makes a transition to some state in the shell II of kinetic energy $w+h\nu$. If this electron is emitted, it appears outside with a momentum characteristic of the shell III of kinetic energy $u=w+h\nu-w_a=\epsilon+h\nu$. The transition II→III is represented by a vertical line, since the retarding force is normal to the surface. Hence only absorption transitions to that part of II which is covered by the indicated parallel projection of III result in photoelectric emission. The discussion in the following has been limited to frequencies for which $h\nu<w_a$. We shall denote by α the kinetic energy associated with the momentum component normal to the surface inside.

[3] Sommerfeld, Zeits. f. Physik **47**, 1 (1928).

Case (a) Fowler's 1st assumption:[4] P_k=const.

$$\sum_{\epsilon,\, d\epsilon} P_k = \text{const. } d(w^{\frac{1}{2}}) = \text{const. } (u+w_a-h\nu)^{\frac{1}{2}}du, \quad (4)$$

$$f(u) = C_1(u+w_a-h\nu)^{\frac{1}{2}}/(e^{(u-h\nu-\epsilon_0)/kT}+1) \quad (5)$$

or $$f(u) \sim F(u-h\nu) \quad \text{if} \quad u \ll w_a - h\nu. \quad (6)$$

This assumption is not consistent with the rule regarding the transition II→III. The results were found by Fowler not to represent experimental data on the total emission, and this assumption was therefore rejected.

Case (b) Fowler's 2nd assumption[4]

$$\sum_{\epsilon,\, d\epsilon} P_k = \text{const. } (w^{\frac{1}{2}} - (w_a - h\nu)^{\frac{1}{2}})dw. \quad (7)$$

This result is obtained, if the light absorption affects the momentum component perpendicular to the surface only, and if P_k is constant for all states within that part of I which is covered by the projection of III—for all other states: $P_k = 0$.

$$f(u) = C_2\frac{(u+w_a-h\nu)^{\frac{1}{2}} - (w_a-h\nu)^{\frac{1}{2}}}{e^{(u-h\nu-\epsilon_0)/kT}+1} = \frac{C_2(w_a-h\nu)^{\frac{1}{2}}}{e^{(u-h\nu-\epsilon_0)/kT}+1}\left\{\frac{1}{2}\frac{u}{w_a-h\nu} - \frac{1}{8}\left(\frac{u}{w_a-h\nu}\right)^2 + - \cdots\right\} \quad (8)$$

or $$f(u) \sim uF(u-h\nu), \quad \text{if} \quad u \ll w_a - h\nu. \quad (9)$$

This case is illustrated in momentum space by the first diagram of Fig. 1. The transition probabilities are indicated qualitatively by the density of the transition lines. That these lines must be vertical—no change of momentum components parallel to the surface!—can be shown to be required by wave mechanics not only for the square top potential barrier, which represents the surface in the Sommerfeld model, but for any kind of surface potential which is a function of the coordinate perpendicular to the surface only. Case (b) is the one mostly used in recent years for determining work functions from saturation current measurements by the so-called Fowler method.

Case (c) DuBridge's assumption[5]

$$\sum_{\epsilon,\, d\epsilon} P_k = \text{const. } ((w+h\nu)^{\frac{1}{2}} - w_a^{\frac{1}{2}})(w/(w+h\nu))^{\frac{1}{2}}dw. \quad (10)$$

In this case[6] the transitions take place radially in momentum space and with uniform density, so that $\sum_{\epsilon,\, d\epsilon} P_k$ is proportional to the volume of the emitting part of I, see Fig. 1.

$$f(u) = C_3\frac{(u+w_a)^{\frac{1}{2}} - (w_a)^{\frac{1}{2}}}{e^{(u-h\nu-\epsilon_0)/kT}+1}\left(\frac{u+w_a-h\nu}{u+w_a}\right)^{\frac{1}{2}} = \frac{C_3(w_a-h\nu)^{\frac{1}{2}}}{e^{(u-h\nu-\epsilon_0)/kT}+1}\left\{\frac{1}{2}\frac{u}{w_a} - \frac{u^2}{w_a}\left(\frac{3}{8w_a} - \frac{1}{4(w_a-h\nu)}\right) + - \cdots\right\} \quad (11)$$

or $$f(u) \sim uF(u-h\nu), \quad \text{if} \quad u \ll w_a - h\nu. \quad (12)$$

It has occasionally been stated, somewhat inaccurately, that this theory is based on the same assumptions used by Fowler in case (b).[7] As a matter of fact the picture of the absorption process is quite different in the two cases, but the final expressions for $f(u)$ are the same to a good approximation for small energies of the emitted electrons.

Case (d) Fowler's 3rd assumption[4]

$$\sum_{\epsilon,\, d\epsilon} P_k = \text{const. } dw\int_{w_a-h\nu}^{w} \frac{d\alpha}{\alpha^{\frac{1}{2}}(\alpha-w_a+h\nu)^{\frac{1}{2}}} = \text{const. } dw \ln\frac{w^{\frac{1}{2}} + (w-w_a+h\nu)^{\frac{1}{2}}}{(w_a-h\nu)^{\frac{1}{2}}}. \quad (13)$$

[4] Fowler, Phys. Rev. **38**, 45 (1931).

[5] DuBridge, Phys. Rev. **43**, 727 (1933).

[6] This refers to the approximate expression for ν "not too far from the threshold ν_0" given by DuBridge, which is the one exclusively used in later work by this author and by Roehr. DuBridge obtains this approximation from a general equation deduced for the velocity distribution, Eq. (25) of his paper. According to the process proposed by DuBridge, I believe that this equation should have a factor $v^2/4(v^2+\xi_\epsilon^2)^{\frac{1}{2}}$ instead of $\xi - \frac{1}{2}[1-\xi_\epsilon/(v^2+\xi_\epsilon^2)^{\frac{1}{2}}]$. Granted this, the general equation of DuBridge calls for $\sum_{\epsilon,\, d\epsilon} P_k$ = const. $D(w)(w+h\nu-w_a)(w/(w+h\nu))dw$ which, except for the "transmission coefficient" D, also leads to the relation (12) above.

[7] The situation is correctly stated in the report by Darrow, Rev. Sci. Inst. **4**, 467 (1933).

In this case (see Fig. 1) the transitions are "vertical" as in (b), but P_k is assumed to be inversely proportional to the normal component of momentum with which the electron will appear outside, i.e., proportional to $(\alpha-w_a+h\nu)^{-\frac{1}{2}}$.

$$f(u)=\frac{C_4}{e^{(u-h\nu-\epsilon_0)/kT}+1}\ln\frac{(u+w_a-h\nu)^{\frac{1}{2}}+u^{\frac{1}{2}}}{(w_a-h\nu)^{\frac{1}{2}}}=\frac{C_4}{e^{(u-h\nu-\epsilon_0)/kT}+1}\left(\frac{u}{w_a-h\nu}\right)^{\frac{1}{2}}\left(1+\frac{1}{12}\frac{u}{w_a-h\nu}-+\cdots\right) \quad (14)$$

or
$$f(u)\sim u^{\frac{1}{2}}F(u-h\nu), \quad \text{if} \quad u\ll w_a-h\nu. \quad (15)$$

Case (e) Mitchell's theory[8]

A quantum-mechanical calculation of the transition probabilities has been given by Mitchell for the Sommerfeld model with a square top potential barrier. Two cases were considered. In the first a constant amplitude was assumed for the vector potential of the radiation field. The result, illustrated in Fig. 1, is that only "vertical" transitions occur and

$$P_k=\text{const.}\frac{\alpha(\alpha-w_a+h\nu)^{\frac{1}{2}}}{((\alpha+h\nu)^{\frac{1}{2}}+(\alpha-w_a+h\nu)^{\frac{1}{2}})^2}, \quad (16)$$

so that
$$\sum_{\epsilon,\,d\epsilon}P_k=\text{const.}\,dw\int_{w_a-h\nu}^{w}\frac{\alpha^{\frac{1}{2}}(\alpha-w_a+h\nu)^{\frac{1}{2}}d\alpha}{((\alpha+h\nu)^{\frac{1}{2}}+(\alpha-w_a+h\nu)^{\frac{1}{2}})^2} \quad (17)$$

and, with the substitution $\beta=\alpha-w_a+h\nu$,

$$f(u)=\frac{\text{const.}}{e^{(u-h\nu-\epsilon_0)/kT}+1}\int_0^u\frac{\beta^{\frac{1}{2}}(\beta+w_a-h\nu)^{\frac{1}{2}}d\beta}{((\beta+w_a)^{\frac{1}{2}}+\beta^{\frac{1}{2}})^2}$$

$$=\frac{C_5u^{\frac{1}{2}}}{e^{(u-h\nu-\epsilon_0)/kT}+1}\left\{1-\frac{3}{2}\left(\frac{u}{w_a}\right)^{\frac{1}{2}}+\frac{3}{5}\frac{u}{w_a}\left(2+\frac{1}{2}\frac{w_a}{w_a-h\nu}\right)-+\cdots\right\} \quad (18)$$

or
$$f(u)\sim u^{\frac{1}{2}}F(u-h\nu), \quad \text{if} \quad u\ll w_a. \quad (19)$$

Mitchell has also calculated the transition probability on the assumption that the (complex) amplitude of the vector potential is constant in the metal, but changes discontinuously at the boundary to a different, constant value outside, the relation between the two being that given by the classical theory for a metal of refractive index $n-ik$. This introduces an additional factor in the expression (16), depending on n,k, the polarization and the angle of incidence, as well as on α or β. For radiation incident near the normal this factor, expressed as a function of β, is:

$$[\beta+w_a-h\nu-(k^2-n^2)(h\nu-\beta)+2nk((\beta+w_a)(h\nu-\beta))^{\frac{1}{2}}]^2$$
$$+[2nk(h\nu-\beta)+(k^2-n^2+1)((\beta+w_a)(h\nu-\beta))^{\frac{1}{2}}]^2.$$

With such values of n and k as are mostly found, this factor does not change a great deal near $\beta=0$ for ordinary values of w_a and $h\nu$, so that the distribution would still be similar to (18) in this case.

Tamm, Schubin[9] and Blochinzew[10] have also published a wave-mechanical treatment of this problem. They obtain for the transition probability

$$P_k=\text{const.}\frac{\alpha(\alpha+h\nu)(\alpha-w_a+h\nu)^{\frac{1}{2}}}{((\alpha+h\nu)^{\frac{1}{2}}+(\alpha-w_a+h\nu)^{\frac{1}{2}})^4}, \quad (20)$$

which leads to the same limiting form (19) for small u.[11] The calculation of Tamm, Schubin

[8] Mitchell, Proc. Roy. Soc. **A146**, 442 (1934).
[9] Tamm and Schubin, Zeits. f. Physik **68**, 97 (1931).
[10] Blochinzew, Physik. Zeits. d. Sowjetunion **1**, 781 (1931).
[11] A similar result was obtained for a somewhat different model by Fröhlich, Ann. d. Physik **7**, 103 (1930). See also Sommerfeld and Bethe in Geiger-Scheel, *Handbuch der Physik*, second edition (1933), Vol. 24/2, p. 468.

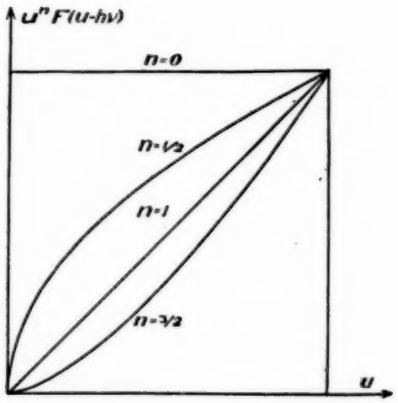

FIG. 2. Theoretical energy distributions for $T=0$.

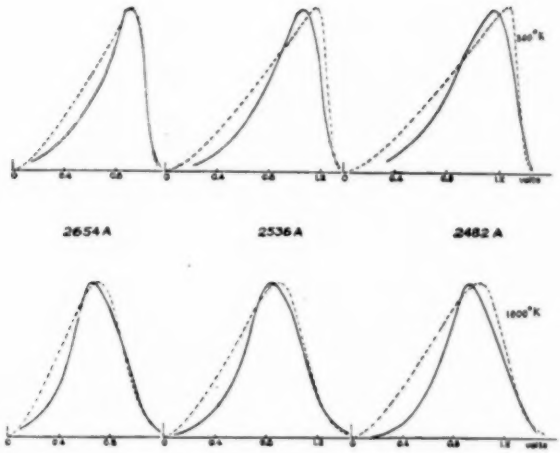

FIG. 3. Energy distributions for molybdenum.

and Blochinzew has been discussed in the paper by Mitchell. It is also interesting to note that an expression for the transition probability somewhat similar to these, namely,

$$P_k = \text{const.}\,\frac{(\alpha+h\nu)^{\frac{1}{2}}(\alpha-w_a+h\nu)^{\frac{1}{2}}}{((\alpha+h\nu)^{\frac{1}{2}}+(\alpha-w_a+h\nu)^{\frac{1}{2}})^2} \qquad (21)$$

has been suggested by Young and Frank,[12] from a different picture of the photoelectric process. They assume that only "vertical" transitions take place entirely inside the metal, all with the same probability. The high energy electron resulting from such a transition inside eventually impinges on the surface, where it is either reflected or transmitted. The expression (21) gives the probability of transmission.[13] Because of the factor $(\alpha-w_a+h\nu)^{\frac{1}{2}}$ this expression will also lead to (19).

COMPARISON WITH THE RESULTS OF W. W. ROEHR

In recent years the variation of the photoelectric yield with frequency has been determined under high vacuum conditions for several metals, with very carefully prepared surfaces.[14] There are, however, very few results available for the velocity distribution, obtained under equally well-controlled conditions. The best energy distribution measurements are probably those for molybdenum published by Roehr,[15] working with DuBridge. Roehr determined stopping potential curves for the emission with (essentially) a spherical condenser arrangement, using monochromatic radiation of three different wavelengths, 2654A, 2536A and 2482A. The temperature of the emitter was varied from 300 to 1000°K. The results were compared with the theory of DuBridge, in which the stopping potential current is obtained from (12) by integration. From the properties of the Fermi function (2) it is easily seen that under these conditions

$$\frac{1}{(kT)^2}\int_{eV}^{\infty} f(u)du = C\cdot\int_{u/kT=eV/kT}^{\infty}\frac{u}{kT}F(u-h\nu)d\left(\frac{u}{kT}\right)$$

will be a function of the variable eV/kT denoted by x, with the parameters C and $(h\nu+\epsilon_0)/kT=x_0$. Near the value x_0 this function can be written approximately as $C\cdot xG(x_0-x)$, with G a universal function which can be evaluated. Roehr plots his experimentally determined $\log(I/x)$ against x at constant temperature and compares this with the curve for $\log G$. He finds that the latter can be fitted to the points obtained for any of the three wave-lengths at 300 and 1000°K by a proper parallel shift, as illustrated by Fig. 8 and Fig. 9 of Roehr's paper. The required shift

[12] Young and Frank, Phys. Rev. **38**, 838 (1931).
[13] Nordheim, Zeits. f. Physik **46**, 833 (1928); Frank and Young, Phys. Rev. **38**, 80 (1931).
[14] See Hughes and DuBridge, *Photoelectric Phenomena* (McGraw-Hill, 1932).
[15] Roehr, Phys. Rev. **44**, 866 (1933).

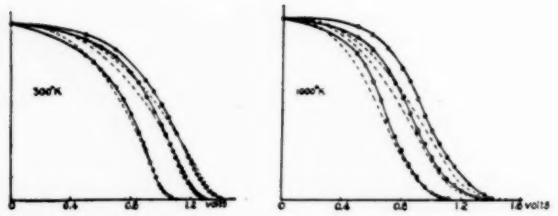

FIG. 4. Stopping potential curves for molybdenum.

along the x axis determines x_0; the procedure is very similar to that of the Fowler method in the case of saturation currents. The conclusion is, that DuBridge's theory predicts quite accurately the form of the photoelectric energy distribution curves in the vicinity of the maximum energy.

In Fig. 2 the limiting form of $f(u)$, *viz.* $f(u) = \text{const.}\, u^n F(u-h\nu)$, for small u is shown at $T=0$ for the five cases (a–e) discussed above: Eqs. (6), (9), (12), (15) and (19), with $n=0$, 1, 1/2 and 3/2. Those parts which correspond to energies less than the critical value $(h\nu+\epsilon_0)$ remain essentially the same for finite values of T, since $F=1$, practically. The experimental curves for the energy distribution are indicated by full lines in Fig. 3, reproduced from Roehr's Fig. 11 and Fig. 12. From a comparison of Fig. 2 and Fig. 3 it should be evident that (a) and (d) are definitely excluded. Of the others, which represent the facts in a rough way, Mitchell's theory, indicated by the dotted lines in Fig. 3, comes nearest to an approach to the experimental curves, although the fit is far from perfect. Roehr's data seem to require a value of n greater than 3/2, something like 2 or 5/2. It is true that the experimental curves cannot be very accurate, since they were obtained from measured stopping potential curves by differentiation. The uncertainty would be greatest in the steep parts for high energies, particularly in the curves for the lower temperature. There could be no doubt, however, that the differences for low energies are real. This should be evident from Fig. 4, in which the points and the solid lines were reproduced from Roehr's stopping potential curves in Fig. 4 and Fig. 5 of his paper. The dotted lines represent the curves calculated on Mitchell's theory.

It should be stated that the accurate expression (18) has been used throughout for $f(u)$ in

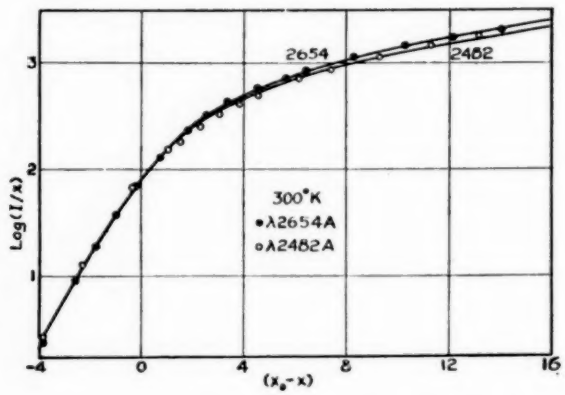

FIG. 5. Analysis of stopping potential measurements at 300°K.

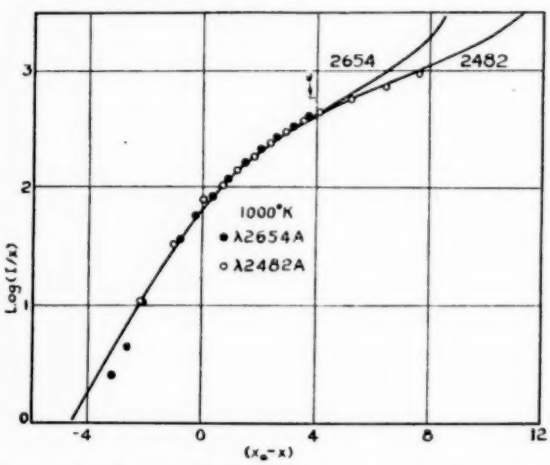

FIG. 6. Analysis of stopping potential measurements at 1000°K.

the curves based on Mitchell's theory, Figs. 3, 4, 5 and 6. Thus $\sum P_k$ is not simply proportional to u^n, as in the approximate expression (19) or the one used by DuBridge, (12). I have computed $\sum P_k$ as a function of u by graphical integration, using the values $w_a=14$ and $w_a-h\nu=9$, both in electron volts, for all three frequencies. As a matter of fact, for the range in question $0<u<1.5$, $\sum P_k$ is rather insensitive to changes in these parameters. The values used for $h\nu+\epsilon_0$, which enters in $F(u-h\nu)$, were those found by Roehr in each case.

It is interesting to see how the theory of Mitchell compares with the experimental data when plotted as log (I/x) against x, as in Roehr's Fig. 8 and Fig. 9. This has been done in Fig. 5 and Fig. 6 for the longest and the shortest

wave-lengths used by Roehr and temperatures 300°K and 1000°K. The points are Roehr's measured values, the solid lines represent the curves to be expected by using the form (16) for P_k given by Mitchell. The curves have been displaced parallel to themselves to produce the best fit, as in the method used by Roehr. The fact that there is a different curve for each wave-length is of course not a feature characteristic of Mitchell's theory alone. On the assumption used by DuBridge the curves calculated from (11) or (12) are really different for different wave-lengths in a way similar to this.

The agreement in Fig. 5 and Fig. 6 appears to be about as good as that found by Roehr on comparison with the curve of DuBridge. This, I believe, illustrates a point which has not always been clearly recognized, although there is good evidence for it already in the paper by Fowler.[4] The fact that a good agreement is obtained with logarithmic plots like these or like the ones used in the Fowler method shows that the state of all the electrons must be described by an antisymmetric wave function (exclusion principle), so that the distribution of electrons over the available single electron levels will be given by the Fermi function. But it proves very little about the correctness of the model used. Thus Fowler found it very difficult to decide whether his 2nd or 3rd assumption was the better one, from comparison with the experimental data, using logarithmic plots. The great value of these methods then lies in the fact that they permit an accurate determination of the work function (Fowler method) or of u_m, the maximum energy of escape if the electron temperature were 0, in the stopping potential method. In the latter case the essence of the method is, that it provides a means of recognizing, in curves for different frequencies, the contributions of electrons that originated in the same energy level in the metal —which is necessary for a photoelectric determination of h. It must be borne in mind, however, that the horizontal shift of the theoretical curve required to fit the experimental data is not entirely independent of the expression chosen for the quantity $\sum P_k$, and this sets a limit to the accuracy of the work function or u_m determined by these methods, until we know the correct form of $\sum P_k$.

Evidently the part of the energy distribution which will prove or disprove something about the model is not the high energy end, where practically all other features are masked by the very rapid variation of the Fermi factor, but the low energy part, where this factor is constant. It seems desirable to obtain more data on the energy distribution in this region by some direct differential method, so that the inaccurate procedure of differentiating stopping potential curves could be avoided. An attempt in this direction is now being made in this laboratory.

The fact that the experimental energy distribution falls below the one predicted by DuBridge in the region of low energy is attributed by Roehr to a transmission coefficient less than unity in this region, a possibility already discussed by DuBridge.[5] This explanation is, of course, not in conflict with the original assumptions on which DuBridge's calculations are based. It is characteristic of the Sommerfeld model, however, that the electrons are entirely free inside the metal and therefore not capable of absorbing radiation. Only at the surface is there a binding and hence a possibility of light absorption, as emphasized by Tamm and Schubin and others. In directions parallel to the surface the electrons are still effectively free and hence unable to absorb, which is the reason why the transitions must be "vertical." Since therefore the photoelectric process for this model actually takes place in the surface of the metal, the entire effect of the potential barrier must be included in the transition probability P_k and there is evidently no place for an additional transmission factor in this case.

Further discussion of the remaining discrepancy between theory and experiment as regards the energy distribution for the photoelectric emission had perhaps better be postponed until more experimental material is available. It is possible that the fit could be improved, by taking into account the variation of the vector potential with depth near the surface, recently considered by Schiff and Thomas,[16] or if reasonably good approximate solutions could be found for other types of surface barriers than the square top one.

[16] Schiff and Thomas, Phys. Rev. **47**, 860 (1935).

The Role of Space Charge in the Study of the Townsend Ionization Coefficients and the Mechanism of Static Spark Breakdown

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The mechanism of spark breakdown has been investigated largely by the study of the deviations of the pre-spark current from the simple electron ionization law $i=i_0e^{\alpha d}$. The deviations indicate a greater current than this for large d. The customary explanation has been that ionization by positive ions occurs or that additional electrons are liberated from the cathode by photoelectric processes or by ion bombardment. We have studied the possibility of increased current being caused, not by a new process, but by a distortion of the field of the spark gap by space charge, giving an apparent increase in the exponential coefficient, α. The coefficient α is a function of the field strength in the gap, but the function consists of three distinct parts. When the field strength is in its lowest range of values, α increases exponentially with field strength; in the middle range, α increases as the square of the field strength; in the third region α increases more slowly than the first power of the field strength. It is shown by solution of Poisson's equation that space charges can occur, that they *will* cause an increase in α in the first two regions but not in the third, that the deviation of α from a constant value in a particular case due to field distortion occurs very sharply as d increases, particularly so in the first region, and that a sparking condition occurs if the original, applied field strength is not so high that local distorted fields extend into the third region. The effect of space charge is only difficultly separable from the other (Townsend) ionization phenomena which may occur, when the field strength is up in the second region, but it is probably the primary cause of spark breakdown in the first region. The Townsend processes are undoubtedly completely valid in the third region.

DURING the past eight years there have been observed results whose interpretation indicated that in some cases at least static spark breakdown of a gap at atmospheric pressures necessitated the assumption of the formation of space charges. In Townsend's[1] original study of the coefficients for ionization by electrons (α) and by positive ions (β) or the equivalent at the cathode (γ), the results indicated no space charge distortion whatsoever. These experiments were carried on at low pressures (about a mm of mercury) and at short electrode distances d, (of the order of 1 cm or less). In most of these measurements the ratio of field strength in volts/cm to pressure in mm Hg (X/p) was high (200 to 1000) for the molecular gases where β was studied. His source of ionization was also relatively weak. In recent years the development of high voltage techniques made it possible to extend such studies to nearly atmospheric pressure and to much larger plate distances. Consequently results were obtained by Paavola[2] and in this laboratory by Sanders[3] which caused some concern. Paavola observed apparent upward curvatures in his plots of log i/i_0 against plate distance yielding an apparent Townsend coefficient at $X/p=36$ to 40 just before breakdown at atmospheric pressure in air. The values of β from these curves appeared to decrease with X/p instead of increase, and it is of interest to note that the value of i_0 was also reduced as the values of X/p increased. Sanders observed a β appearing at X/p in air of above 110 while Townsend's results gave 160 as the critical value. Again, Sanders' values of β varied erratically as a function of X/p. Recently, D. Posin, working in this laboratory on Sanders' outfit observed in measurements to be reported elsewhere that the appearance of β was not only a function of X/p and p but depended on plate distance d, the intensity of ultraviolet illumination i_0, and that the value of β/p around X/p 110 to 200 varied over a given curve by as much as a factor of four or five. This disconcerting discovery led the writers to conclude that in this case there was a space charge distortion of the field taking place due to positive ion accumulation near the cathode, and that such a distortion could lead to an apparent increase in the value of α for the applied field which might be mistaken for Townsend's β. In order to test this the differential equation below applicable to this case was

[1] J. S. Townsend, Nature **62**, 340 (1900); Phil. Mag. **2**, 598 (1903).
[2] M. Paavola, Archiv f. Elektrotechnik **22**, 443 (1929).
[3] S. H. Sanders, Phys. Rev. **41**, 667 (1932); **44**, 1020 (1933).

set up and integrated. The equations obtained make it possible to analyze what occurs for different field strengths, plate distances, pressures, and photoelectric ionization and indicate beyond a doubt that the results of Paavola, Sanders and Posin can be accounted for on this basis. It furthermore makes it seem probable that static spark breakdown in the molecular gases at adequate pressures and gap lengths is primarily initiated by a space charge mechanism. At low pressures there is little probability of this occurring, and the mechanism depends on a true β or γ as Townsend assumed. In the intermediate region both factors play a role. In any case the space charge does not preclude some action at the cathode (β or γ) occurring before breakdown in all cases, except that at higher pressures the space charge precedes and makes possible the secondary process.

The critical feature in all this process is, we discovered, the nature of the curve for Townsend's α/p as a function of X/p. Graphic differentiation of Sanders and Posin's curves for α/p as a $f(X/P)$ indicates at least three different ionization mechanisms existing, to wit, one where α/p is proportional to e^{BX} at very low X/p (20 to 40), a second where α/p is nearly proportional to $A(X/p-b)^2$ (40 to 150) and a transition point where α/p approaches constancy. The calculations to follow will show that the first type of variation leads to rapid space charge formation with a very unstable regime going readily over to a spark for very small voltage fluctuations. The second one leads to the type of results observed by Posin, while in the third regime above $X/p=200$ the space charge mechanism is eliminated and we have the well-known Townsend regime. It is interesting to note that this will probably explain the transition with pressure from a regime where sparking potential is dependent on electrode material to one where it is electrode material independent.

The Treatment of the Space Charge Equation

Two parallel plate electrodes enclosed in a tube are separated a distance d and are raised, respectively, to potentials O and V_d. The cathode is illuminated with ultraviolet light which liberates photoelectrically a current of electrons i_0. The i_0 electrons proceed through the gas toward the anode producing by ionization further electrons and their associated positive ions. At any point in the gas a distance x from the cathode, the electron current is given by $i_-=i_0e^{\alpha x}$ where α is the electron ionization coefficient. The current reaching the anode is thus $i_-=i_0e^{\alpha d}$. From the condition of continuity, that the total current crossing any plane parallel to the electrodes must be a constant, we get at once that $i=i_++i_-$. There are no positive ions crossing the plane of the anode, so the total current is just $i=i_-=i_0e^{\alpha d}$. Substituting in $i=i_++i_-$ we have $i_0e^{\alpha d}=i_++i_0e^{\alpha x}$ giving i_+ as $f(x)$

$$i_+=i_0(e^{\alpha d}-e^{\alpha x}).$$

To determine the effect of space charge we must solve Poisson's equation for this case: $\nabla^2V=-4\pi\rho$. Since the current flow is unidimensional and consists of both positive and negative charges this reduces to: $d^2V/dx^2=-4\pi(\rho_+-\rho_-)$. By using the equations

$$j=\rho v;\quad v=kX \qquad (v=\text{velocity},\quad k=\text{mobility})$$

and $X=-dV/dx$ and inserting the values of i_- and i_+, we get

$$\frac{d(dV/dx)}{dx}=-\frac{4\pi j_0}{dV/dx}\left(\frac{e^{\alpha d}-e^{\alpha x}}{k_+}-\frac{e^{\alpha x}}{k_-}\right),$$

where j_0 is the electron current density at the cathode and is used instead of i_0 because Poisson's equation is expressed in terms of charge density.

Since k_+ is only 10^{-4} of k_-, $1/k_-$ may be neglected with respect to $1/k_+$, giving

$$\frac{dV}{dx}\cdot\frac{d(dV/dx)}{dx}=-\frac{4\pi j_0}{k_+}(e^{\alpha d}-e^{\alpha x})$$

or

$$XdX/dx=-(4\pi j_0/k_+)(e^{\alpha d}-e^{\alpha x}).$$

Now α/p is a function of X/p, or at constant pressure, $\alpha=f(X)$. In the derivation of the equation $i_-=i_0e^{\alpha x}$ it was assumed that X was uniform throughout the electrode gap, which is not the case if the field is distorted by space charge. We cannot, therefore, write $i=i_0e^{\alpha d}$ because α is not a constant throughout d. We must write instead of $e^{\alpha x}$, $\exp(\int_0^x\alpha dx)$ and in place of $e^{\alpha d}$, $\exp(\int_0^d\alpha dx)$. The equation to be

solved then becomes

$$XdX/dx=$$
$$-(4\pi j_0/k_+)(\exp(\textstyle\int_0^d \alpha dx)-\exp(\int_0^x \alpha dx)).$$

Make two substitutions:

Let $\int_0^x \alpha dx = u$, then $du/dx=\alpha$. Replace $j_0 \exp(\int_0^d \alpha dx)$ by its equivalent, j.

Then $XdX=(4\pi/k_+)(j_0e^u-j)dx=(4\pi/k_+)(j_0e^u-j)du/\alpha$, or $\alpha XdX=(4\pi/k_+)(j_0e^u-j)du$.

Note that while j is dependent on u and X, in any particular experiment in which d and X are not changed, j will be a constant for it is not a function of x.

We thus get

$$\int_{X_0}^{X}\alpha X dX=(4\pi/k_+)\int_0^u(j_0e^u-j)du.$$

In the range of values of X/p from 40 to 180 for N_2 gas, where the relation of α/p to X/p is parabolic, it is sufficient to make the following approximation over a small region:

$$\alpha/p=A'(X/p)^2 \quad \text{or} \quad \alpha=AX^2.$$

Inserting this value of α,

$$\int_{X_0}^{X}\alpha X dX=A\int_{X_0}^{X}X^3dX;$$

$$\therefore \quad (A/4)(X^4-X_0^4)=(4\pi/k_+)(j_0e^u-ju-j_0).$$

We thus have an expression for X as a function of u

$$X^4=(16\pi/Ak_+)(j_0e^u-ju-j_0)+X_0^4,$$

in terms of two *unknown* constants, j and X_0. We have two equations for determining them:

$$du/dx=\alpha=AX^2;$$

$$\therefore \qquad \int_0^{\log(j/j_0)}du/AX^2=\int_0^d dx \qquad (1)$$

and

$$X=-dV/dx, \quad \therefore \quad \int_0^d Xdx=-\int_0^V dV, \qquad (2)$$

and since $dx=du/AX^2$ we have

$$\int_0^{\log(j/j_0)}du/AX)=V_d=X_Ad,$$

where X_A is the applied field. By inserting the value of X above,

$$\int_0^{\log(j/j_0)}\frac{du}{[(16\pi/Ak_+)(j_0e^u-ju-j_0)+X_0^4]^{\frac{1}{4}}}=Ad,$$

$$\int_0^{\log(j/j_0)}\frac{du}{[(16\pi/Ak_+)(j_0e^u-ju-j_0)+X_0^4]^{\frac{1}{4}}}=AX_Ad.$$

These two equations must be solved in the following manner:

Given a value of j_0, the applied field X_A, and d; find the corresponding values of j (or j/j_0) and X_0. We want j as a function of d. Since the quadrature cannot be performed directly, the method of solution is one of trial and error, using numerical integration on a tried value of X_0 and j and seeing if X_A and d are obtained correctly.

Note that in these equations it is the current density and not the total current which enters. Thus a current of 10^{-12} amp. may leave the cathode, but if this current only comes from one square mm of surface, the current density will be 10^{-10} amp. per cm^2.

A sample calculation was made on the following assumptions:

$$j_0=1.75\times10^{-11} \text{ amp.}, \quad X_A=120 \text{ volts/cm}, \quad p=1 \text{ mm}.$$

The value of α for the undistorted field was 1.00. Plotting $\log(j/j_0)$ against d showed that at $d=7.96$ cm, $\log(j/j_0)=8$, and at $d=8.6$ cm the slope of the $\log(j/j_0)$ *vs.* d curve became infinite (a suitable condition for a spark).

As mentioned above, the increase of α as the field is distorted depends on the functional relation of α/p to X/p. If the function α/p increases faster than X/p, $(\alpha/p=f(X/p))$, then it can be shown in a simple way that $\log(j/j_0)$ will increase above its value when the field is undistorted. Similarly, when α/p increases more slowly than X/p, the space charge can no longer give an apparent large value of α but must give a smaller value. This may be shown as follows: (taking $\alpha=AX^2$ first).

We had two equations to satisfy,

$$\int_0^d \alpha dx=A\int_0^d X^2dx=\int_0^{\log(j/j_0)}du=\log(j/j_0), \qquad (3)$$

$$\int_0^d Xdx=X_Ad. \qquad (4)$$

If there is a uniform field X_A, $\log(j/j_0)=\alpha_0 d$, α_0 being a constant. We must show whether the value of $\log(j/j_0)$ obtained from the first integral

is greater or less than $\alpha_0 d$ under the condition imposed by the second integral.

Shift the X axis to X_A; then $\int_0^d X dx = \int_0^d (X' + X_A) dx$, which by (2) $= X_A d$.

Now $\int_0^d X_A dx = X_A d$. $\therefore$ $\int_0^d X' dx = 0$. There is thus as much area above X_A as beneath X_A; i.e., X' is part negative and part positive. $\int_0^d X^2 dx$ becomes $\int_0^d (X' + X_A)^2 dx = \int_0^d X'^2 dx + 2X_A \int_0^d X' dx + \int_0^d X_A^2 dx$. Noting that $\int_0^d X' dx = 0$

$$A \int_0^d X^2 dx = A \int_0^d X'^2 dx + A X_A^2 d = A \int_0^d X'^2 dx + \alpha_0 d.$$

Since $X'^2 > 0$ this shows that $\log (j/j_0)$ will be greater than $\alpha_0 d$.

If α should equal AX, it is obvious that $\log (j/j_0)$ will be unchanged by space charge. If $\alpha = AX^n$ and $n > 1$, $\log (j/j_0)$ will increase; if $n < 1$, $\log (j/j_0)$ will decrease. Since $\alpha/p = f(X/p)$ corresponds to $n > 1$ for X/p up to 180 in N_2 and 130 in air and corresponds to $n < 1$ above 180 and 130, respectively, space charge can explain an apparent increase in α above α_0 only on the lower side.

The solution indicates the following facts:

Depending on the number of molecules present in a given spark gap, with sufficient illumination, a value of X/p great enough to cause ionization by collision will give rise to space charge formation of such magnitude as materially to distort the curves of $\log (i/i_0)$ plotted against d, and in such fashion that they resemble the curves of β or γ observed at low p by Townsend. Furthermore, this apparent space charge distortion can lead to an ultimate breakdown of the gap without the intervention of a β, provided the field distortion does not become so high as to bring α/p into the third region of variation with X/p. It is probable that in the first region of variation of α/p with X/p, i.e., when $\alpha/p = Ae^{BX/p}$, which occurs for X/p around 40, space charges can be built up for values of j_0 of an extremely low order. Hence there exists under these conditions, with sufficient gap length, an exceedingly unstable condition. With such instability it becomes experimentally practically impossible to study the curvature of the $\log (i/i_0)$ *vs.* d curves before spark breakdown occurs in view of the fluctuations of the high potential source and the extreme sensitivity to variations in X/p. Paavola seems to have been the only one to observe this curvature and must be congratulated on the steadiness of his potential source. Whether local fluctuations in cathodic emission of electrons due to cosmic-ray bursts or dense local electron emission can produce current densities under these conditions sufficient to cause a spark is a matter of speculation. If they can, the statistical time lags, etc., can be nicely accounted for.

In the lower pressure regime, at high X/p, in which the experimental work initiating this investigation was performed and where α/p varies as $(X/p)^2$ the equation has been completely solved. In this region measurable upward curving of $\log (i/i_0)$ *vs.* d curves will occur at $X/p = 120$ in N_2 for a current density j_0 of 2×10^{-11} amp./cm^2 and a plate distance of 7.5 cm, and the spark will appear at 8.1 cm. The values obtained in Posin's experiment fit these criteria. Using an estimated density of 10^{-15} amp./cm^2 Posin observed a true and constant β with no sign of space charge distortion. With a current density estimated at about 10^{-12} amp./cm^2 at $X/p = 120$ Posin observed an α showing signs of space charge distortion, i.e., β was not constant. Because of the nonhomogeneous nature of the focused image of the quartz mercury arc it is impossible accurately to evaluate j_0. These estimates are therefore only approximate and to this degree of approximation appear to fit the equation. This indicates that extreme care must be used in this region in interpreting the experimental results obtained, and a very careful study of the conditions, using a photoelectric emission of controlled and uniform nature, is definitely required. The results of Posin indicate quite clearly that in this pressure region apparently both the appearance of a real β or γ and a space charge distorted α may occur simultaneously. Hence in this region the sparking mechanism may be exceedingly complex. In this region, however, because of the slower variation of α/p with X/p it becomes possible experimentally to observe in more detail the deviation of the $\log (i/i_0)$ *vs.* d curve from a straight line. Even here, however, when space charge effects occur, the curvature is so sharp that a spark occurs very shortly after the initiation of the departure from linearity. When a true β occurs in this region one can follow the curvature over a

far greater length of curve before the spark breaks. In this region of p and X/p it is doubtful whether a spark could be initiated due to space charge with inadequate illumination, and it is probable that because of the importance of the β with lower illumination, both values of β and sparking potential will be dependent on electrode material.

In the third regime, which with few exceptions is the regime in which Townsend worked, we can expect no space charge effects and the existence of a true β or γ.[4] This is due to the fact that α/p varies linearly with or even more slowly than X/p. In this region if a γ-mechanism is active we would expect to find the apparent value of β deduced from the curvature of the log (i/i_0) *vs.* d curves and the sparking potential to be a function of electrode material. For the sparking potential this is borne out by the experiments of L. J. Neuman in argon. Experiments are now in progress in this laboratory to determine both these points. It must be noted that the discussion here given probably applies to all gases of a molecular nature in which the rate of gain of energy of the electrons follows the course characteristic of N_2 and air. This may not be exactly the case in the inert gases where elastic electron impacts change the functional relation of α/p as a function of X/p.

[4] Note that in this paper, wherever we refer to Townsend's β we are not committing ourselves as to whether the β is caused by ionization by positive ions in the gas (true β) or whether it is due to photoelectric liberation of electrons or liberation of electrons by positive ions on impact with the surface of the cathode (Townsend's γ). We incline, however, to the belief that it is the γ-type of phenomenon which causes the effects observed owing to the high energy required for ionization by positive ions in the gas.

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Photoionization in Gases

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The balanced space charge positive ion detector, used in the experiments on ionization by positive alkali ions has been used in the study of photoionization in gases. The following experiments were performed: (1) A hydrogen discharge tube, operated by either a 1000- or an 8000-volt transformer, was set up so that the radiation emitted could pass through a fluorite window into one of the space charge ion detectors. The detector contained the gas to be ionized at 0.02 mm pressure. When the pressure in the discharge tube was lowered to about 5 mm or less, the character of the discharge changed noticeably, and ionization was observed, but it was definitely proved that all ionization that occurred was of electrostatic origin, despite careful shielding, and was not caused by the radiation. It is believed that this may explain to some extent the ionization of gases observed by Lenard, for he used an intense high frequency spark as a light source. N_2, A, Xe, and air were tried in this tube. (2) An apparatus similar to that used by Mohler was used in which electrons of energies up to 150 volts were allowed to ionize the gas at one end of the tube and the resulting radiation to ionize the same gas at the other end in one of the balanced space charge cylinders. As observed by Mohler, photoionization of A by its own radiation was found, but this disappeared when a fluorite window was inserted. The same was true in xenon gas. Since xenon has a metastable level near 1500A, this experiment seems to eliminate the possibility of ionization being produced by the absorption of two quanta, each having a fraction of the necessary energy. No ionization of N_2 by its own radiation was observed with or without the fluorite window. This is analogous to Mohler's non-observance of ionization of H_2. Similar results were observed in air.

EXPERIMENTS carried on in the Physical Laboratory at the University of California by Dr. A. M. Cravath indicated that an important mechanism in the development of spark breakdown of gases might consist of photoelectric ionization in the gas and also perhaps at the cathode surface as a result of the excitation of the atoms by electron impact in fields approaching breakdown strength. Cravath reported that a highly absorbable radiation was capable of ionizing air at atmospheric pressure. At the time from the absorption measurements he believed that

this radiation might have a wave-length of approximately 1200A. He drew this conclusion from what absorption data exist in oxygen for short wave-lengths and from a statement in Hughes and DuBridge's *Photoelectric Phenomena*, page 273 ff, in which Hughes cites experiments purporting to show that ionization could be caused in air by wave-lengths of the order of magnitude of 1250A. Earlier experiments by Lenard also seemed to bear upon this point. It seemed to us that since the ionization potentials of the principal constituents of air lie far below this 1250A limit, it might be worth while to investigate the question further. We felt that it was particularly appropriate to investigate this question in view of the extreme sensitivity for positive ion detection in gases yielded by the balanced space charge method of Edlefsen and Lawrence,[1] and modified by Varney.[2] The detector was the one used for the study of ionization by positive alkali ion impact in inert gases as described elsewhere. It could be highly evacuated and any purified gas readmitted. Since the tube operated best at gas pressures of 10^{-2} mm Hg, this pressure was used. A liquid-air trap was kept connected with the tube at all times when readings were being taken. In the experiments when air was used in the detector, oxide-coated filaments were used in the space charge cylinders to supply the electrons for the space charge.

The experiments were conducted at first so as to attempt to verify the results of Hughes. For this purpose the source of radiation was a pear-shaped tube with the two electrodes consisting, respectively, of a wire inside a capillary and a wire loop outside and adjusted so that the capillary pointed toward the ion detector. It was separated from the detector by a fluorite window, filled with H_2 gas at variable pressure, and operated either from a 1000- or an 8000-volt transformer run at $\frac{1}{4}$ kw. The transmission limit of the fluorite was very kindly measured for us on the vacuum spectrograph by Dr. H. P. Knauss. The last line that was observable on the plate was at 1340A, so the limit was probably at about 1300.

No ionization was observed in any gas when this source was used except that when the pressure of H_2 in the discharge tube was less than about 6 mm, ionization of some sort of electrostatic origin was observed. The discharge tube and the transformer were enclosed in a grounded metal box with only a $\frac{1}{4}$-inch hole, covered with a wire gauze, for the light to enter the detector. In spite of this screening, the ionization in the detector could only be completely stopped if the window too was covered with metal soldered to the rest of the shield. This phenomenon was always observed when the discharge tube pressure was so low that the visible plasma reached the window. The nature and thickness of the window also influenced this ionization. When a glass window was used, the pressure had to be about half that for a fluorite window before ionization was observed. Very thin quartz windows, made of bubbles blown on the end of a fused quartz tube, were tried, and with these ionization began at about the same pressure as with an 0.8-mm piece of fluorite. Whatever the mechanism is which is involved here, it adds another likely explanation of the "photoionization" observed by Lenard, with his high frequency aluminum spark and his metal ionization chamber, to the one given by Hughes and DuBridge. It seems unlikely that this accounts for the ionization observed by Hughes whose experiments were conducted at atmospheric pressure in the detecting chamber were a discharge induced in the gas could not occur. Hughes found ionization occurring only for *one specimen of fluorite*, and it broke before he made a measurement of its transmission limit. It is conceivable that it was a freak piece with a considerably lower limit than 1250A, or perhaps, since it was very thin, that it was porous in some spots. Since he had no liquid air on the gas, two highly important impurities may have been present. Mercury, either condensed on the glass and acting as a sensitive photoelectric surface or becoming ionized itself by the radiation, would give a misleading result. When air is exposed to intense ultraviolet light it is found to contain a considerable amount of NO gas. Since this gas has an ionization wave-length of 1300A it could be ionized by the light, and since the air is exposed to ultraviolet light the NO might easily be present, especially at higher pressures in the detecting chamber. Since the effect was only observed with this one specimen of fluorite it,

[1] Lawrence and Edlefsen, Phys. Rev. **34**, 233 (1929).
[2] Varney, Phys. Rev. **47**, 483 (1935).

however, seems more logical to assume it to have been due to a flaw in the fluorite. Other observers have reported similar effects. Of these the work of Palmer[3] may be ruled out on account of Hg and the others because they used Lenard's type of apparatus. In this connection attention might be called to the experiments of Oldenberg[4] on the fluorescent spectrum of N_2. Oldenberg found that if he inserted a *10^{-5}-cm film of collodion* between the irradiated gas and the original light source, that *the entire fluorescent spectrum, both of ionized and neutral N_2 disappear completely*. The film was known to transmit to between 1200 and 1300A. Our results are in agreement with this and in disagreement with those of Hughes.

The second source used was similar to that used by Mohler in his work by this same general method on photoionization of gases. It was simply an arrangement to accelerate electrons in a gas with any desired energy from 0 to 150 volts. This tube was connected directly to the detector, and the fluorite window could be moved in and out of the path of the light beam. In argon and xenon, strong photoionization was observed when the electron energy exceeded the ionization potential of the gas and the window was not in place, but the ionization disappeared, or certainly decreased by a factor greater than 10^4 when the window was inserted. The fact that *no ionization was observed in xenon seems to rule out the possibility of the ionization being caused by two successive quantum collisions because xenon has a metastable level well within the observed transmission limit of the fluorite.*

When air or N_2 were used in this tube, only very weak ionization was observed without the window, none was observed with the window. It will be remembered that Mohler was unable to observe ionization of H_2, even in absence of a window, by this process. It is estimated that the balanced space-charge method increases the sensitivity of the unbalanced method by a factor of about 10^3.

It seems, therefore, from our experiments, that in pure, clean, dry gases photoionization by radiation of energy *materially* less than the ionization potential of the gas is highly unlikely. It has been found by numerous observers in the case of the alkali vapors that ionization occurs for many lines of the principal series, and thus at energies less than the ionization potential. The results were many of them obtained by the space-charge method and are thus beyond question. In these cases, however, the thermal energy of agitation of the gas molecules due to the temperature and the use of hot filaments, as well as the energy of the electrons in the space charge is adequate for the realization of many mechanisms by which the deficit of energy (in any case not exceeding 0.3 volt) may be made up.

The results reported for ionization of mercury by 2536A radiation in a sense approach more nearly the question raised in this paper. However, it need merely be pointed out that the 2536 line produces a metastable state in mercury whose average life is probably the longest (perhaps with the exception of helium) on record. In addition, λ2536 is probably as readily absorbed by resonance in mercury as any line in the metal vapors in this region. Thus the phenomenon in question, i.e., photoionization at wave-lengths well below the ionization threshold, could occur more favorably here than in any other circumstances. It certainly does not appear to happen in the case of gases like H_2, N_2, air, or the inert gases in any reasonably measurable amount.

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[3] Palmer, Phys. Rev. **32**, 1 (1911).
[4] Oldenberg, Zeits. f. Physik **38**, 370 (1926).

Effects of High Shearing Stress Combined with High Hydrostatic Pressure

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Mean hydrostatic pressures up to 50,000 kg/cm² combined with shearing stresses up to the plastic flow point are produced in thin disks confined between hardened steel parts so mounted that they may be subjected to normal pressure and torque simultaneously. Qualitative and quantitative studies are made of the effects of such stresses. Among the qualitative effects it is found that many substances normally stable become unstable and may detonate, and conversely combinations of substances normally inert to each other may be made to combine explosively. Quantitatively, the shearing stress at the plastic flow point may be measured as a function of pressure. The shearing stress at plastic flow may rise to the order of 10 or more times greater at 50,000 kg/cm² than it is normally at atmospheric pressure; this is contrary to the usually accepted results in a narrower range of pressure. If the substance undergoes a polymorphic transition under these conditions of stress, there may be a break in the curve of shearing stress *vs.* pressure. This gives a very convenient tool for the detection of transitions. 57 elements have been explored in this way, and a number of new polymorphic transitions found.

INTRODUCTION

THE experimental study of high stresses has hitherto been confined almost exclusively to high hydrostatic pressure. The distortion produced by hydrostatic pressure is simply describable, and the physical effects are specifiable in terms of a few parameters. Greater complications may be expected if shearing stresses are allowed to act in addition to the hydrostatic pressure. It is, I think, the general feeling that these additional complications are probably of inferior physical significance, but that this may be too narrow a point of view is suggested by the fact that the forces between molecules are in general certainly not central forces, so that on the molecular scale any except the simplest solids must be the arena of shearing forces of high intensity. Furthermore, if such a phenomenon as molecular disintegration by high stress is possible, it is probable that shearing stresses will be much more effective than hydrostatic pressure.

The intensity of the shearing stresses hitherto realizable in practice has been restricted to a rather low value; there is no intrinsic upper limit to the hydrostatic pressure to which a substance may be subjected, but the shearing stress may not exceed a certain limit set by plastic yield of the material. The first plastic yield point in shear may be very low, as shown by the behavior of single crystals of many of the metals. The effect of initial plastic flow is to raise the resistance to plastic flow, a phenomenon described as "work hardening." It is known that this work hardening cannot proceed beyond a somewhat nebulously defined upper limit, and that there is a roughly defined "upper yield point" and a maximum shearing stress supportable by any material. In an ordinary tensile test the tension is accompanied, on planes at 45° to the direction of the principal tension, by a shearing stress numerically equal to one-half the tensile stress, so that under these conditions rupture or plastic flow occurs when the shearing stress reaches one-half the tensile stress limit. This quantity has been measured for many metals and rises higher than a few thousand kilograms per square centimeter for relatively few substances. Engineers have found that under the limited conditions of engineering practice the maximum shearing stress is not greatly affected by a superposed hydrostatic pressure, so that ordinary engineering experience would suggest that it would be impossible under any conditions to apply to a material a shearing stress of much more than one-half its ultimate tensile strength. This opinion is sometimes explicitly expressed in criteria of rupture.

This expectation, however, rests on a narrow range of experimental conditions, and it turns out that by sufficiently raising the mean hydrostatic pressure the maximum shearing stress may be very considerably increased. In the following are described experimental means by which this may be accomplished, as well as some of the effects of such high shearing stresses. This paper must be regarded only as a suggestive

introduction to the subject; given the method of producing the stress, many sorts of experiment will occur to any one, some of which I have tried and will publish later, and some of which I have not yet had time to try. The results described in this paper fall into two parts; first a purely qualitative description of the behavior of a number of chemical compounds, and secondly a quantitative examination of the behavior of all the available elements. It is characteristic of the method that it is applicable to very small quantities of material, so that it has been possible to examine more of the elements than is often possible.

Description of Method

The principle of the method is suggested by Fig. 1. *A* represents a thin disk of the material under examination, squeezed between two cylinders *B* and *C* of hardened steel, with accurately ground plane ends. If the material *A* is softer than the hard steel it will, if its initial thickness exceeds a critical value, flow out laterally until the thickness of the disk is reduced to such a value that the friction against the steel near the outer edge of the disk is sufficient to balance the mean hydrostatic pressure exerted on the central parts of the disk. It is obvious that if friction is finite, lateral flow must eventually cease, no matter how great the pressure exerted by the cylinders *B* and *C*. When the equilibrium thickness has been reached for a given mean pressure, a couple is applied to the cylinders *B* and *C* with respect to each other. The initial effect of the couple is to produce a slight angular displacement, resisted by elastic distortion in the cylinders and in *A*, but if the couple is high enough, *B* rotates with respect to *C* with uniform angular velocity. There is thus applied to the disk *A* a shearing stress, the maximum magnitude of which is determined by the force necessary to produce uniform rotation of *B* and *C*. Under this maximum shearing stress there may either be slip at the surfaces of separation of *A* from *B* and *C*, or more usually plastic flow throughout the interior of *A*. In the following only the effects of the maximum shearing stress, that is, the effects when there is uniform rotation of *B* with respect to *C*, are studied.

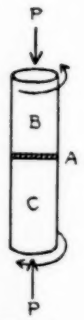

Fig. 1.

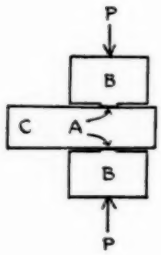

Fig. 2.

Fig. 1. Idealized apparatus for exerting pressure and shearing stress simultaneously on the thin disk at *A*.

Fig. 2. Scheme of the actual apparatus. The material in the form of a thin disk at *A* is squeezed by a hydraulic press pushing the steel cylinders *B* against the anvil *C*, which is rotated, while the cylinders *B* are held stationary by friction against the press.

In actual application, the apparatus is considerably modified from the simple scheme represented in Fig. 1. In the first place the maximum pressure attainable with the scheme of Fig. 1 would be limited to very materially less than the maximum compressive strength of the steel as given by ordinary compressive tests because of longitudinal splitting of the cylinders due to friction of *A* as it flows out laterally. By proper design of the steel parts, it is possible, however, to exceed very materially the ordinary compressional limit of the steel.

Local intensities of stress, which are very much greater than the intensities attainable under more normal conditions, are often reached in parts of a system which receive proper support from surrounding parts. Consider, for example, the Brinell method of measuring hardness by measuring the dimensions of the indentation produced by a hardened steel ball. Formulas will be found in the engineering handbooks for the stresses in the ball under working conditions. It appears that steel balls are regularly used on hard materials up to a compressive force at the point of contact of 75,000 kg/cm², about twice the compressive strength under ordinary conditions of test. It is obvious in this case that the area of the ball receiving the maximum thrust is supported by surrounding parts of the ball and of the material with which it is in contact, and rupture prevented.

The arrangement adopted in the following by which the surrounding parts support the most

highly stressed parts, is something like that of the Brinell hardness test. The upper cylinder *B* of Fig. 1 is replaced by a very short boss projecting from a very much larger piece of steel. This boss is referred to in the following as the "piston"; in most of the experiments the diameter of the face of the piston was 0.25 inch, although 0.375 and 0.50-inch pistons were also sometimes used. The lower cylinder *C* of Fig. 1 is replaced by a large block of steel with a perfectly flat face, referred to in the following as the "anvil," and the material *A* is placed between the two. Finally, in order to eliminate frictional resistance to the rotation when the couple is applied, the whole arrangement is doubled, as shown in Fig. 2, and the anvil is rotated between the two pistons, which themselves do not rotate. The two pistons are compressed together with any desired force with a hydraulic press, and the force required to rotate the anvil is measured with a simple strain gauge on the handle of the rotating wrench. By doubling the apparatus, not only is end thrust eliminated, but each experiment is made virtually the mean of two, with a corresponding greater certainty in the results.

In setting up the apparatus it was necessary to use various auxiliary devices to ensure accurate centering and proper placing of the material of the disk, which need not be described in detail. Suffice it to say that the apparatus must be well made; all the parts must be accurately centered and aligned.

As a matter of routine the mean pressure exerted by the pistons was carried in all the following experiments to a maximum of 50,000 kg/cm². The success of the piston in withstanding this pressure depends to a certain extent on the nature of the compressed material; many of the softer materials produce no perceptible effect on the piston except a slight rounding of the very outer edge, whereas the harder materials may produce much greater damage, grinding scratches in the surface, and sometimes chipping pieces off the edge along shear planes at approximately 45°. There was almost always some perceptible permanent alteration of the piston, so that a fresh set of pistons was used for every experiment, either completely new pistons or pistons reground after a former experiment. A freshly ground part of the anvil was also always used for each new experiment. The necessity of fresh parts for every experiment makes the small size of the apparatus a very real advantage.

The maximum force to produce rotation, and therefore the maximum shearing stress applicable to the disk, varied greatly from substance to substance; the maximum reached for any substance was 18,000 kg/cm²; the force on the end of a 1-meter lever to produce this was about the limit of what one man wanted to exert.

The actual distribution of stress and strain in the disk is evidently very complicated, and must differ greatly from the mean values just discussed. An exact solution of the problem would be impossible to give, both because of mathematical difficulties arising from the finite size of the strains, and because of physical difficulties arising from the fact that the constants of the material vary in an unknown and important way at such high stresses. However, some qualitative idea of the distribution of stress and strain can be obtained from the conventional solution of Hertz by the methods of classical elasticity theory, assuming small strains and unaltered elastic constants. This solution will be discussed in more detail in another paper, which will go into all questions of technique in greater detail. The solution shows that the originally plane surfaces of the anvil do not remain plane, but it becomes relatively depressed at the center, so that under stress the disk assumes the shape of a double convex lens, sometimes as much as five times as thick at the center as at the edges. The actual thickness of the disks in these experiments after exposure to a mean pressure of 50,000 kg/cm² was of the order of a few thousandths of an inch, being greater than 0.005 inch at the center only for a few of the hardest materials. Not only is the strain distribution far from uniform, but the normal pressure is not uniform, being greatest near the outer edge of the disk. Since the greater part of the area is concentrated near the outer edge, the assumption of mean values for normal pressure and also for shearing stress, the latter calculated on the assumption of a constant coefficient of friction all the way across the disk, gives a rough idea of what is happening. The attempt to get more accurate values than that

corresponding to mean values must be left until later, if indeed it proves feasible at all.

Experimental Results

1. Qualitative results

This whole study of the effect of shearing stresses was the outgrowth of the extension of measurements on polymorphic transitions to 50,000 kg/cm², which will be described in a subsequent paper, and in particular was at first directed to the attempt to produce in other substances irreversible and permanent changes analogous to the change from white to black phosphorus. It seemed not unreasonable that if the atoms or molecules could be forced to slide over each other by a shear they might take up new positions which they would be less likely to assume under the uniform distortion of a hydrostatic pressure. It seemed that perhaps sulfur was the most likely candidate for an irreversible change to a metallic modification, because of its chemical similarity to phosphorus. An irreversible transition from graphite to diamond was also an attractive possibility, made plausible by the magnitude of the volume change, and the fact that the diamond structure can be approximately obtained from the graphite structure by a shear and an axial compression. The anticipated permanent changes were not produced, however. It then suggested itself that substances in which the molecular and atomic forces are not as intense as in sulfur and carbon, as in the more loosely knit organic compounds, might show permanent changes; the first substance tried of this kind was rubber. Positive results were at once obtained; rubber is derubberized to a hard translucent material, not unlike horn in appearance. Paper was also transformed into a translucent horn-like mass. By control experiments it was established that the paper was not transformed by the action of a pure hydrostatic pressure of 50,000, but the rotation was necessary for the effect. Wood and linen cloth next showed a similar sort of transformation. Celluloid was then tried; it detonated violently, blowing off the edges of the piston. One disk detonated spontaneously when a pressure of 25,000 was reached without rotation, but the full 50,000 and rotation in addition was necessary to detonate the other disk. This result was perhaps not surprising in view of the known unstable character of celluloid.

The detonation of celluloid brings up the question of temperature changes, there must of course be a local rise of temperature during rotation; the question is whether it is large enough to be important. An upper limit to the rise of temperature can at once be found from the known solution of the following problem in one-dimensional heat flow: The X axis is maintained at temperature 0 for all negative values of time. At the origin of time a source emitting unit quantity of heat per unit time is installed at the origin and constantly maintained for positive times. The known solution gives for the temperature at the origin $(t/\pi\kappa\rho)^{\frac{1}{2}}$, where κ is thermal conductivity, ρ specific heat, and t the time.

In the shearing experiments the rate of generation of heat by friction was of the order of 5 g cal. per sec. Taking for the specific heat of steel 0.1×0.28, and for the thermal conductivity 0.15×0.28, in appropriate units, where 0.28 is the cross section of the piston, the rise of temperature at the end of five seconds, the maximum time of rotation, is 37°C. This value must be too large by a factor of several-fold, because actually heat flow takes place from the region of generation three-dimensionally into a practically infinite mass, instead of one-dimensionally as assumed here. The thermal factor thus appears to be of absolutely no importance in the following results.

After the experiments already described, NH_4NO_3 was tried, with the expectation that it would detonate even more readily than celluloid, but no effect could be obtained by the full 50,000 and repeated rotation. Red phosphorus was then tried; this was irreversibly transformed into black, a result which was checked by determining the density by the flotation method, and was also kindly checked by Dr. Jacobs, who found that the x-ray structure is the same as that of the high density black phosphorus. There are at least two varieties of black phosphorus.[1] Previous attempts to transform red to black phosphorus by the application

[1] R. Hultgren, N. S. Gingrich and B. E. Warren, J. Chem. Phys. 3, 351 (1935).

of hydrostatic pressure alone up to 50,000 had not been successful. The cooperation of the shearing stress is apparently necessary for the transition, and is the sort of thing that I had been looking for in the beginning.

One of the obvious difficulties of these experiments was to determine with the very small amounts of material available whether there really was any important permanent change. A determination of density by the flotation method offered possibilities, but unfortunately the density of most of the substances is outside the range of this method. It seemed to me that color changes might afford a sensitive indication, particularly in the case of certain organic substances like the dyes, and the next substance tried was accordingly thymol blue. This showed no change of color, but did show a striking change of solubility, becoming so insoluble in slightly acidified water as to color the water by only a barely perceptible amount. Rosanilin, on the other hand, showed no perceptible change. Professor Forbes of the Chemistry Department then suggested to me that PbO_2 would be an interesting substance because of the different colors of the different oxides. To my great surprise this detonated violently, leaving a residue of metallic lead. The yellow oxide, PbO, was next tried; on compression to 50,000 it rotated quietly, but on releasing pressure it was found completely decomposed to a film of metallic lead.

It thus appeared that important effects of shearing stress were not confined to complicated organic compounds, and a number of inorganic compounds which suggested themselves for one reason or another and which were readily available in the casual laboratory stock, were rapidly tried. These experiments were superficial to the extent that I made no attempt to analyze the resulting product, but in most cases recorded only whether there was a detonation or not. These experiments will be summarized presently.

The question next presented itself whether certain compounds could not be synthesized. The first attempt was made with copper and sulfur, it having been found previously that CuS is not affected. The results were at once positive; there was a detonation at about 20,000 without rotation, and the product was apparently the ordinary black sulfide. A few other syntheses were next tried. First the thermite reaction, Fe_2O_3+Al; there was a very violent detonation between 20,000 and 30,000, without rotation, and with much damage to the steel parts; the product of the reaction was apparently metallic iron. $K_2C_2O_4+Al$ was compressed to 50,000 and after considerably more rotation than usual one of the disks detonated, but the other could not be made to detonate by prolonged rotation. Examination showed that the detonation had been confined to the peripheral parts of the disk, where the intensity of stress is greatest, and that the central parts were unaltered. Ground quartz, SiO_2, +Mg filings, in the ratio of 24 Mg to 60 SiO_2 by weight, detonated on one side after several rotations at 50,000, but the other disk did not detonate. The whole behavior was much like that of $K_2C_2O_4+Al$. Finally a mixture of powdered silicon and MgO was similarly detonated on one side, the other side being obdurate; this detonation was of more than usual violence, about one-half the piston being blown away. This completes the list of syntheses attempted to date; the subject is a most inviting one and nearly inexhaustible. I have now made provision to continue this sort of exploration, with microanalysis of the resulting products.

The various qualitative experiments to date are briefly summarized in Table I.

TABLE I. *Summary of qualitative experiments on effects of high shearing stress and high hydrostatic pressure.*

I. Substances giving negative results

Graphite, both amorphous and single crystal, mica, NH_4NO_3, sugar, rosanilin, CuS, SiO_2, tremolite, NH_4F, CuO, MgO, Ag_2S, Fe_2O_3, LiF, AgCl, $K_2C_2O_4$, $NaBrO_3$, Si, Rochelle salts, $HgNO_3$, $K_2Cr_2O_7$.

II. Substances which detonate

Celluloid, CHI_3, PbO_2, $KMnO_4$, Ag_2O, MnO_2, $(NH_4)_2Cr_2O_7$, $AgNO_3$, $Sr(NO_3)_2$, $Cr_2(SO_4)_3K_2SO_424H_2O$, $Cr_2(SO_4)_3K_2SO_4$, $Al_2(SO_4)_3$, $CuCl_22NH_4Cl2H_2O$.

III. Substances showing other sorts of positive results

Rubber, changes to a horn-like substance; "Duprene," somewhat like rubber; wood, changes to a horn-like translucent substance; paper, changes to a horn-like translucent substance; linen cloth, changes to a horn-like translucent substance; Brom thymol blue, no change in appearance, but becomes insoluble; Se, amorphous variety partially changed to metallic; S, crystalline variety probably changes to amorphous; PbO, no detonation, but decomposes to metallic Pb; HgO, the red modification changes to black; P, red changes to the dense black modification.

IV. Combinations with detonation

Cu + S, Fe_2O_3+Al, SiO_2+Mg, $K_2C_2O_4+Al$, Si+MgO.

2. Quantitative experiments

The quantitative experiments consisted of a determination of the force required to rotate as a function of mean normal pressure, and were restricted to those substances which showed no permanent change. Interesting information may be expected from the curve plotting rotating force against pressure, both because this sort of phenomenon has previously been very little studied, and because the pressure range is considerably greater than that yet open to experiment. The most obvious and immediate information from curves of this kind is with regard to polymorphic transitions; if the shearing strength of one polymorph is different from that of the other a break in the curve may be expected on passing the transition pressure. Great advantages of this method of exploring for polymorphic transitions are that the quantities of material necessary are very small, 0.1 g or less, and that it is very rapid, a complete exploration up to 50,000 and back to zero in steps of 2000 occupying less than one hour. Further, the method does not depend on the volume change, so that transitions with too small a volume change to detect by the more conventional volumetric methods may be discovered in this way. Of course, it is not impossible that conversely two polymorphs with a large volume difference should be so nearly alike in shearing strength as to give no indication by the shearing method, but it happens that none such, or at most one such, has been found. A disadvantage of the method is that the results are not as accurate as by the volume method, for the reason that the stresses throughout the disk undergoing transition vary so much from point to point that the transition is spread over a range of mean stress rather than confined to a single stress of discontinuity. Also, to date, the shearing method has been applied only at room temperature, although there is no intrinsic reason why it should not be applied at other temperatures.

The quantitative use of the shearing method as a supplement of the volumetric method was checked at first on bismuth, which had already been found to have polymorphic transitions near 25,000 at room temperature. In Fig. 3 is shown the force required to produce rotation as a function of the mean normal pressure. The

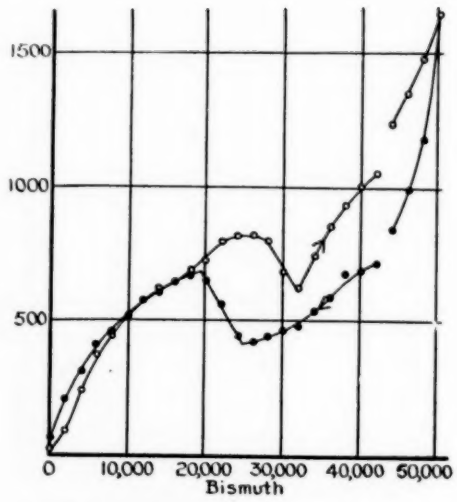

FIG. 3. The curve of shearing stress of bismuth in kg/cm² (ordinates) against mean hydrostatic pressure in kg/cm² (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure. The breaks in the curves indicate polymorphic transitions.

transitions known to occur in the neighborhood of 25,000 are accompanied by a drop in the shearing force; there are in reality two transitions here at not very different pressures, but the sensitiveness of the shearing method is not great enough to resolve them. In addition, Fig. 3 shows distinct breaks, both with increasing and decreasing pressure, in the neighborhood of 42,000, suggesting another transition at this point. Previous exploration by the volumetric method had failed to reveal any new transitions beyond 25,000, but reexamination of the data now showed that there had been a discontinuity of volume in the neighborhood of 42,000 which had been discarded as without significance because of its smallness. More careful repetition of the volumetric measurements verified the reality of this new transition, and a determination was successfully made of the approximate transition parameters as a function of temperature, which will be described in another paper.

An additional advantage of the shearing method is that a transition is much less likely to be suppressed because of internal viscosity than when the stress is a hydrostatic pressure. An interesting example is antimony; this is similar chemically and in crystallographic properties to bismuth, so that high pressure polymorphism would be expected, but at higher pressures than

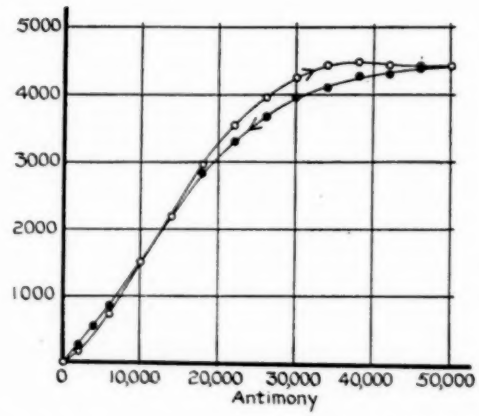

FIG. 4. The curve for antimony of shearing stress in kg/cm² (ordinates) against mean hydrostatic pressure in kg/cm² (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure. It is probable that the flat maximum with increasing pressure indicates the beginning of a transition analogous to the first transition of bismuth.

for bismuth because the melting point of antimony is so much higher than that of bismuth. Volumetric examination had failed to disclose any such transition up to 50,000. Shearing measurements, however, gave a curve which flattens off in the neighborhood of 50,000 exactly like the flattening off of the curve for bismuth in the neighborhood of 25,000, as shown in Fig. 4, and I believe that there is practically no doubt but that at 50,000 or higher antimony has transitions analogous to the transitions of bismuth near 25,000.

In interpreting the results of the shearing explorations for polymorphism, account must be taken of the effect of shearing stress as such on the transition temperature (or pressure). There is no general rule as there is for a melting temperature, the melting temperature of a sheared solid being always less than that of the unsheared solid, but depending on the relative elastic constants of the two solid phases the transition temperature at constant pressure of a sheared solid may be either raised or lowered. Judging, however, from the transitions studied thus far by both methods, the effect of shearing stress on transition temperature is not large in the majority of cases in actual practice, so that a rather close estimate of the pure hydrostatic pressure necessary to produce the transition at a given temperature can usually be made from the shearing measurements.

All the available elements, 57 in number, were systematically examined for polymorphism by the shearing method up to 50,000 kg/cm². The method is obviously not restricted to elements, and the next step on the program is to extend it to compounds.

The majority of the elements are not polymorphic at room temperature up to pressures of 50,000; nevertheless, even in these cases the information afforded by plotting rotating force as a function of pressure is of intrinsic interest, and we next consider what is the significance of these results.

As the normal pressure on the disk increases, three more or less distinct stages are to be recognized. First, at very low pressures, the material of the disk slips over the face of the steel pistons, as in conventional experiments made to determine the ordinary coefficient of solid friction. In this first stage the stresses are so low that there is no permanent or plastic deformation in either surface, and the friction may be thought of as arising from local elastic deformations as the unevennesses in one or the other surface force aside opposing projections of the other surface. With increasing normal pressure the second stage begins when the elastic limit is exceeded locally; there are now changes in the geometrical configuration of the surfaces, and the coefficient of friction departs from its initial constant value. The local plastic deformations which accompany slip often involve "seizing" or welding of one surface to the other. It seems to be usually the case that the beginning of seizing is accompanied by an increase in the coefficient of friction, but I believe that there is no intrinsic reason, particularly in the case of substances very much softer than steel, why the plastic flow which must accompany seizing should not sometimes result in a decrease of the effective coefficient. The second stage may be thought to end when the normal pressure has become so high that the whole surface has seized, or at any rate is involved in plastic flow, and from here on the material is in the third stage, where shear is brought about by plastic flow distributed more or less uniformly throughout the entire body of the material. Within the range of stress of ordinary engineering practice it seems to be the case, as already stated, that

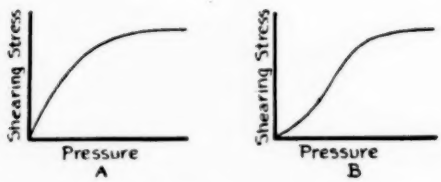

FIG. 5. Illustrates the two types of curve for shearing stress against pressure.

the shearing stress under these conditions of plastic flow is independent of the normal pressure, so that during the third stage the plot of rotating force against normal pressure would be a horizontal line parallel to the pressure axis. From a highly idealized point of view the complete curve of rotating force against normal pressure might be expected to have one of the forms indicated in Fig. 5, depending on whether the transition from the first to the second stage is accompanied by an increase or a decrease of the effective coefficient of friction. The actual curves often depart greatly from this shape, particularly with respect to the horizontal asymptote. Failure to approach a horizontal asymptote is a measure of the failure of shearing stress to be independent of normal pressure, and the very great departure of many of the elements from this behavior is one of the most significant of the results of these measurements.

A simple interpretation of the results is complicated by the deformation of the steel pistons, particularly in the case of the harder metals. With the softer metals the steel does not experience any permanent deformation, but its surface is left intact after the experiment. Some of the softer metals "seize" or weld to the steel almost perfectly, and have to be separated by cutting away with a razor blade; the union is as good as in a perfect soldered joint. For such substances the shearing force obviously gives a perfect measure of the shearing strength for uniform flow in the body of the metal. Even when the soft metal does not weld to the steel surface, slip must involve a large amount of plastic flow, so that the force to produce rotation must be a good indication of the resistance of the metal to shear in bulk. But in the case of the harder metals the interpretation of the results is not so simple. There is almost always a certain amount of welding, but it is confined to a small number of small spots; the disk can almost always be pried away from the anvil with a razor blade as a coherent whole. The surface of the steel is now almost always damaged; there may be microscopic pits or long circumferential scratches. This distortion of the steel is in itself instructive, for it means that the sheared metal has become harder than glass hard steel in some places. This local hardening doubtless involves a more or less complete destruction of the crystal structure. A striking example is afforded by graphite. In the ordinary massive form (Acheson graphite) it is soft enough to be whittled easily with a knife, but after its structure has been broken down by shearing under high pressure and while still under pressure it becomes a most effective abrasive. On one occasion a minute piece of graphite was subjected for 15 hours to a mean pressure of 100,000 kg/cm² by a special arrangement of the surrounding glass hard steel parts so as to afford the maximum of mutual support; the graphite was found partly embedded in the steel, as a diamond might have been forced in, but there was no permanent alteration in the graphite. A result of the ability of many of the harder and stronger materials to receive intense local hardening is that the total rotating force is not a measure of resistance to plastic flow homogeneously distributed throughout the mass, but is a measure of contributions made by only a part of the whole.

The strength of the *steel* is involved in the actual turning force in a complicated way depending on the distribution of the localities of permanent damage to the steel. One may be sure, however, that the shearing strength of the steel to a homogeneously distributed shear is at least as great as the highest shearing force observed for any of the materials. This maximum figure was 18,000 kg/cm², obtained with boron under a mean normal pressure of 50,000 kg/cm². In all other cases, it can be inferred that the shearing strength of the homogeneous metal is as great or greater than that given by the rotating force. The figure obtained in this way, although it is unsatisfactory because it is a lower limit, is, however, very informing in most cases because it is so much higher than the maximum shearing resistance to homogeneous flow at atmospheric pressure. The lower limit

obtained in this way is probably not far from the value for homogeneously distributed flow in those cases where the curve is notably concave toward the pressure axis at the upper end, that is, in those cases where there is a strong tendency toward the expected horizontal asymptote.

The "self-welding" of most of the substances studied is much greater than their welding to the steel. Thus the original material may be in the form of a fine powder or it may be a coiled helix of wire; but the final form after exposure to pressure and shearing was almost always a coherent disk. A few substances, however, do not self-weld at all; these will be noted later. The fact that self-welding is so common suggests that the minimum value of the shearing force discussed in the last paragraph is probably not very far from the true value for homogeneously distributed flow.

The importance of the effect of "cold working" at high pressures may be estimated from the agreement of the curves of rotating force for increasing and decreasing pressure. If an important amount of work hardening is produced by pressures between 30,000 and 50,000 in addition to that produced by the initial pressure of 30,000, then the curve with decreasing pressure will lie above that with increasing pressure, and if such an effect is not important, then the two curves will coincide. In the case of many of the harder metals the work hardening in this range appears to be unimportant.

It is perhaps not surprising that the shearing force at plastic yield is in many cases a strong function of normal pressure when it is considered that the viscosity of liquids has been found to vary more with pressure than any other physical property, and that the nature of plastic yield of a solid as completely disorganized as these solids must be under such extreme stresses must have points in common with viscous slip in a liquid. The effect of pressure on the viscosity of liquids varies enormously with the complication of the molecule, being comparatively small for monatomic mercury, and becoming very large for complicated organic compounds. Similarly, one might anticipate that for monatomic elements the shearing force for plastic flow might not vary greatly with normal pressure, but that in complicated organic compounds the variation

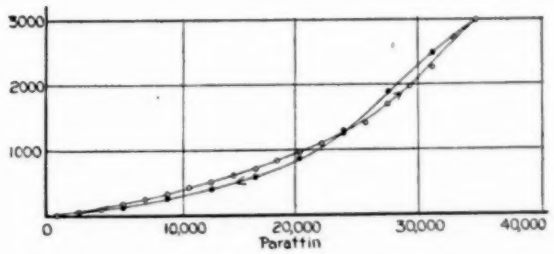

FIG. 6. The curve for paraffin of shearing stress in kg/cm² (ordinates) at plastic flow against mean hydrostatic pressure in kg/cm² (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure.

might be very large. This idea was tested by measuring the rotating force for ordinary solid paraffin as a function of normal pressure; the results are shown in Fig. 6. The shearing strength of paraffin is so low that all observable points on the curve must refer to the third stage of the process described above, that is, the stage of plastic flow throughout the interior of the paraffin. If the shearing stress for plastic flow were independent of normal pressure, then the curve should be a horizontal straight line not higher than the lowest observed point. As a matter of experiment, the highest observed force was 900 times as great as the lowest, so that the shearing force at plastic flow fails to be independent of normal pressure by at least 900-fold. Furthermore, the rate of increase of plastic shearing stress with normal pressure itself increases with pressure, the slope of the curve at the maximum pressure being approximately seven times as great as initially.

In addition to the broad features of the phenomenon just discussed, a number of other considerations are necessary before the complete significance of the results can be estimated. These other features are perhaps best suggested by a description in detail of the experimental procedure. The specimen as originally placed in the apparatus was usually, in the case of the metals, in the form of a disk of approximately the diameter of the piston and of convenient thickness, usually somewhere between 0.010 and 0.030 inch. For nonmetallic elements, a disk was also used when possible, made by compressing the powdered material into a proper form. In some cases the powdered material was placed directly on the piston, and kept in place

by a narrow paper collar. The first stage in the experiment consisted of an initial application of pressure, usually somewhere between 10,000 and 30,000 kg/cm², depending on the nature of the material. The anvil was then rotated back and forth until a steady value of the rotating force was reached; this steady value was always reached from below, the force rising toward an asymptotic value, and the variation during the attainment of the steady value might be as much as 100 percent. The rotation was back and forth through an angle of about 35°, and sometimes a dozen alternations were necessary before the steady value was reached. Pressure was then released to zero, and regular readings were begun. Each point, plotted as in Figs. 3, 4, and 6, is the mean of readings for the two directions of rotation. There usually were consistent differences in the readings for the two directions, the magnitude of which depended on the nature of the material; the softer metals gave very consistent readings in the two directions, whereas with the harder nonmetals, such as graphite, the difference might be as much as 30 percent, or occasionally even more. The reading for one direction of rotation was itself a complicated thing, the turning force passing through a regular pattern of variation. The force to start rotation was usually not the same as the final force; during perhaps the first 10° of the rotation the force would rise from below or fall from above to an asymptotic value which persisted rather closely during the last 25°. It is the mean of the asymptotic values which is plotted in the figures. Sometimes the pattern of variation was more complicated, such as rising to a maximum, falling to a minimum, and then rising to a steady value. In the case of most metals the total range of variation was of the order of 10 percent, but the variation might be much larger for brittle nonmetallic elements.

The initial variations on reversing direction of rotation are doubtless connected with the setting up in the disk of some sort of structure depending on the direction of rotation. The amount of distortion required to reach the steady condition is very considerable, corresponding to a lateral displacement by shear of one face of a cube with respect to the opposite face by an amount of the order of 20 times the side of the cube, the displacement corresponding to the full rotation of 35° being of the order of 60 times the cube side. What the structure is under such extreme conditions it is not easy to say; that there must be more left of the undistorted crystal structure than one might be at first inclined to admit is shown by the fact that the material is capable of exhibiting the same polymorphic transitions that it does under hydrostatic pressure. Doubtless while the rotating force is attaining its steady value there is a reorientation of the planes of slip within the crystal. Recrystallization does not take place in such a direction, however, as to give slip planes in such locations as to reduce the rotating force to a minimum. This was strikingly shown by several experiments in which the disk was initially a piece of single crystal with the slip planes parallel to the face of the pistons; such experiments were made with bismuth, antimony, zinc, and Ceylon graphite. The seasoning effects in these cases are abnormally high, that is, rotation is exceedingly easy as long as slip may take place on planes parallel to the face, but this initial structure is speedily broken up, and the rotating force rapidly rises. This effect was especially marked with single crystal Ceylon graphite, for which the rotating force rose 15-fold during break-up of the regular laminated structure.

The speed of rotation was usually of the order of 10° per second, but no important variation of the force was observed within rather wide limits of variation about this value. In this respect there is a complete contrast with the viscous distortion of a liquid, showing that plastic flow in a solid is a different kind of phenomenon. The fact that the force is independent of the speed is, as already mentioned, a strong argument for believing that the rise of temperature at the surfaces of slip is not an important factor.

There was the greatest difference conceivable between the behavior of an ordinary metal and many of the brittle nonmetals. Rotation in the case of the metals was almost always accomplished quietly and smoothly, but the nonmetals usually emitted grinding and snapping noises, and the rotating force was often very jerky; it might hang at an approximately constant level, but with more or less periodic drops to a

smaller value, rapidly climbing back, or it might periodically jump to a higher value, and almost at once snap back.

In recording the readings the pattern of variation of the rotating force as well as the final asymptotic value was almost always noted, recording the turning points before the steady value was reached. Similar readings were made at regular pressure intervals up to the maximum, and back to zero again. There were almost always differences between the curves with increasing and decreasing pressure. This is to be expected under the conditions; during increasing pressure the disk is being squeezed out laterally from between the pistons and this is being resisted by radial friction. This frictional effect, of course, does not reverse on decrease of pressure; the disk does not suck back into itself material from beyond the pistons, but on the contrary contracts more or less elastically. The elastic deformations in some of the materials under 50,000 must be rather high, and it was in fact not uncommon to find radial cracks in the disk after release of pressure. Further, the pistons almost always suffer some permanent damage from the maximum pressure. In view of these important elements of irreversibility, the degree of accord between increasing and decreasing runs was in general better than I would have expected, and gives evidence that the curves give information about some intrinsic property of the material.

After return to zero pressure the apparatus was dismounted, the thickness of the disks measured, and notes made about the general appearance of the disk and the nature of the permanent damage to pistons and anvil. All in all, it will be seen that the complete record of a single run, although it might occupy less than one hour, embraces many complicated factors, and an exhaustive study of all the significant results which might be extracted from the experiments would be very time consuming. In the following an attempt is made to touch on only the most striking features; critical points in the curves and the increase of shearing stress for plastic flow with normal pressure. In general the materials which are weak and soft under ordinary conditions offer the least resisting force to rotation, and are squeezed out to the thinnest disks.

Measurements were made altogether on 57 elements. About 40 of these were measured with two different pieces of apparatus. The first apparatus differed in details that need not be discussed from the final apparatus shown in Fig. 2; the construction was such that sometimes at the higher pressures part of the force to produce rotation was used in overcoming friction in the apparatus itself. When the importance of this was realized, all the measurements were repeated with the final apparatus, the construction of which allows no friction except between the anvil and disks. The measurements with the first apparatus were not entirely valueless by any means, but afforded welcome confirmation of the main features of the results obtained with the final apparatus.

Extreme purity in the material appears not to be an important factor. This was checked by measurements on copper of commercial and of 99.999 percent purity. This is what might be expected in view of the probable high degree of disorganization of the material while flowing. This is to be contrasted with the fact that the initial yield in a single crystal is highly sensitive to slight impurities.

A relatively large number of the curves show more or less sharp breaks in direction. The interpretation of these breaks requires discussion. In a number of cases I have verified by independent volumetric analysis that these breaks correspond to ordinary polymorphic transitions which occur under pure hydrostatic pressure at a pressure not far from the mean pressure in the shearing experiments. The interpretation of the break in these cases is thus obvious; furthermore the conclusion can be drawn that the transition parameters are not greatly affected by the shearing force. In a number of cases, however, there are breaks in the curves which have not been checked by volumetric analysis. Some of these I hope to examine later by the volumetric method. If the result is negative, it is still possible that there is a polymorphic transition with change of volume too small to detect; many cases of this character should be amenable to an examination by the method of discontinuity of electrical resistance. Until this exami-

FIG. 7. A possible relation between transition temperature and shearing stress. If curves of this type exist, then there may be transitions produced by shearing stress which cannot be produced by hydrostatic pressure alone.

nation has been made, the correct explanation of these breaks must remain in abeyance. Several possibilities in addition to polymorphism must be recognized. In the first place it is barely possible that a break may arise from a sudden change in the mechanism of slip; a corresponding phenomenon is known in single crystals of iron, for example, where beyond a certain stress, slip begins on a new set of planes. The break in all cases of this sort must be a break with decreasing slope of the rotating-force *vs.* pressure curve. There are a few such breaks, but there are also breaks with increasing slope, to which this suggestion cannot apply. It does not seem to me very probable, however, that crystallographic slip planes can play a very important part when the material is so thoroughly disorganized as here, and in any event I should expect the corners of the break to be rounded. A second possibility which I think must be recognized is that the break may mean a new kind of transition, produced by shear only. It is true that all ordinary transitions are affected by shearing stress; if the shearing stress acting on such systems is varied continually to the vanishing point, the transition temperature at a constant hydrostatic pressure varies continuously toward a limiting value. But it need not follow conversely that all transitions which take place under a definite shearing stress at a definite temperature permit a continuous variation of shearing stress to zero; it is conceivable that the relation between shearing stress and temperature might be like that indicated in Fig. 7. This would mean that under shearing stress a type of transition could be brought about not realizable by ordinary methods. Such a possibility does not seem to have been hitherto discussed; it would obviously be difficult to establish under ordinary

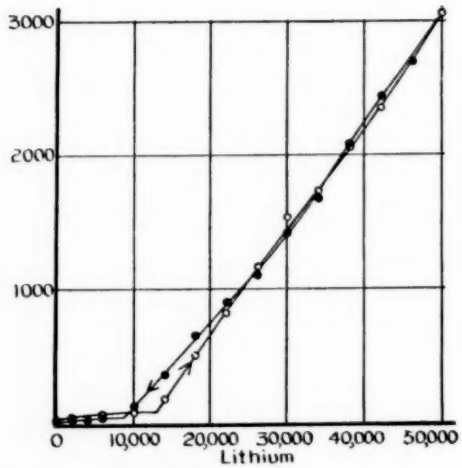

FIG. 8. The curve for lithium of shearing stress in kg/cm² (ordinates) against mean hydrostatic pressure in kg/cm² (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure.

conditions. But I believe that the possibility must be kept in mind; a case in point is lithium, the curve for which is given in Fig. 8. There is a break in the curve at a mean normal pressure of about 12,000 kg/cm². But both the volume and the electrical resistance of lithium have been measured up to hydrostatic pressures of 20,000 and no ordinary transition has been found. It may be that there is an ordinary polymorphic transition at pressures higher than 20,000 at room temperature, and that this pressure is displaced by an unusually large amount by shearing stress, or it may be that there is an ordinary transition not far from 12,000 and that it is suppressed under ordinary conditions by internal viscosity, or finally I believe that the possibility must be kept in mind that we have here a new kind of transition, produced by shear only.

There follows now a brief summary of the results for 57 elements; those showing breaks are given first. The order of presentation appears unsystematic; it was mostly determined by similarities in the nature of the shearing curves, which are not immediately related to more familiar properties. A number of the elements have been found by ordinary volumetric methods to have polymorphic transitions; the detailed discussion of the thermodynamic parameters of these transitions will be given in another paper.

A. Elements showing breaks

Lithium. The curve has already been given in Fig. 8. The experiment was repeated with 3/8-inch pistons, giving a break of the same character and at nearly the same location, and with the same value for the shearing strength, 850 kg/cm², at the maximum pressure reached with the 3/8-inch pistons, which was 22,000 kg/cm². The shearing strength at 50,000 was 3050 kg cm². The almost linear increase of rotating force with normal pressure beyond the break is a notable feature; in so soft a material as lithium the flow must be homogeneously distributed throughout the entire mass, so that this means an almost linear increase with pressure of shearing stress at plastic flow.

Strontium. There are two distinct breaks in direction, both with increasing and decreasing pressure, the interpretation of which probably is a polymorphic transition at a mean pressure in the neighborhood of 25,000 kg/cm². The existence of this transition was not checked by volumetric analysis. Beyond the transition, shearing force against pressure is concave upwards, reaching a maximum value of 2500 kg/cm² at 50,000. This means an enormous increase over the value at atmospheric pressure, since strontium is a relatively soft metal.

Calcium. There appear to be two slight breaks in direction, both with increasing and decreasing pressure. The breaks are so slight that probably no significance would have been attached to them if they had not been qualitatively similar to the much more pronounced breaks in the chemically similar strontium. There is probably a transition at a mean pressure of 30,000 kg/cm²; the volume change at the transition must be small because it was not found by volumetric analysis at −80°. At room temperature the volumetric exploration was not complete. The shearing strength at 50,000 was 1800 kg/cm².

Barium. The relations are very much like those for calcium; there are two slight breaks both with increasing and decreasing pressure, which probably mean a transition near 30,000. Again the transition was not found by volumetric analysis either at −80° or at +150°, so that if the transition exists its volume change must be small, or else the pressure displacement by shearing stress must be abnormally large. The shearing strength at 50,000 was 1200 kg/cm².

Cadmium. This metal I have already found to be polymorphic with two transitions at room temperature near 3000 and 6000 kg/cm². The transitions are unusual in that they could be detected only in single crystals of pure metal; volumetric analysis even with the extremely sensitive apparatus for measuring linear compressibility gave negative results on polycrystalline material. It is therefore very gratifying that with the shearing apparatus, by using 0.5-inch pistons to a maximum pressure of 17,000 kg/cm², very definite breaks were found at a mean pressure of 4300 kg/cm², corresponding closely enough to the mean of the two pressures above. The method does not have a high enough resolving power to split the two transitions. The experiment was repeated with essentially the same results. It is probable that there are no other breaks up to 50,000, but this is not certain because the measurements to 50,000 with 0.25-inch pistons were made only with the first form of apparatus which is somewhat uncertain because of friction.

Zinc. Because of the chemical and crystallographic similarity of zinc to cadmium similar transitions would be expected, but none have hitherto been found. The shearing experiments, however, showed very marked anomalies at the high pressure end of the range, indicating a probable transition in the neighborhood of 40,000. The experiment was repeated with essentially the same results. The shearing strength at 50,000 was 1800 kg/cm² for the first set-up, and 2200 on repetition, enormously higher than the upper limit for severely worked zinc crystals under ordinary conditions. At the low pressure end of the range the curve is concave toward the pressure axis with a rather unusually sharp knee in the neighborhood of 10,000, probably marking the beginning of flow throughout the body of the metal, with a closer approach to constant shearing force beyond this point than shown by most metals.

Vanadium. This material had about 5 percent impurity, and was from the same batch as the former compressibility specimens.[2] Vanadium begins to verge on the nonmetallic in its shearing

[2] P. W. Bridgman, Proc. Am. Acad. **62**, 219 (1927).

properties; rotation did not always take place smoothly, and there were occasional snapping noises. The steel pistons were more scarred than usual, with distinct welding on limited areas. There were very definite breaks in direction both with increasing and decreasing pressure, meaning probably a transition at a mean pressure of 37,000 kg/cm² and a mean shearing stress of 7800 kg/cm². The shearing strength at 50,000 was 13,000 kg/cm², well toward the top of the materials measured. No volumetric analysis was attempted.

Manganese. This is the same material as that whose compressibility and electrical resistance under pressure have already been measured.[3] It was in the form of rods about 0.020 inch in diameter, which were laid together in the form of a grid compactly covering the pistons. There was little or no self-welding or welding to the steel. The rotation was almost perfectly smooth, being thus more metallic in this respect than vanadium. There were very definite breaks in direction (increase of slope) both with increasing and decreasing pressure at a mean hydrostatic pressure of 20,000 kg/cm² and mean shearing stress of 3300 kg/cm². Beyond the break the shearing force increases nearly linearly with pressure, with only slight concavity toward the pressure axis, to a maximum of 4500 at 50,000. This is probably still far below the point of homogeneous distribution of shearing stress.

Antimony. This has already been mentioned; the shearing force passes through a flat maximum at 40,000 with a decline of a few percent at 50,000. The highly probable interpretation is a transition in the neighborhood of 50,000 analogous to the known transition of bismuth. There was practically no welding to the steel. The shearing strength at 50,000 was 4400 kg/cm².

Tellurium. This shows the phenomenon of polymorphism very strongly developed—a strong maximum, decrease, and then a strong rise again, indicating probably two transitions at a mean hydrostatic pressure of 39,000 kg/cm² and mean shearing stress of 3000 kg/cm². The high pressure modification therefore has a lower shearing strength than the low pressure modification. A more detailed discussion will be found in the paper on volumetric analysis. This is a good example of the value of the shearing method to supplement the volumetric analysis; a preliminary volumetric analysis did not disclose anything definitely at room temperature, the volume change being beyond the end of the range at this temperature, but after the very striking evidence given by the shearing measurements the volumetric measurements were repeated and the effect easily found at higher temperatures.

Iodine. The results with this were doubtful. Near 50,000 the curve with increasing pressure rapidly becomes flat, and there is almost a maximum at 50,000. Because of the extreme softness of iodine the shearing stress must have become homogeneously distributed long below 50,000, and the interpretation of a transition seemed plausible. But this interpretation was made doubtful because the curve with decreasing pressure did not reproduce the effect, but was approximately linear with pressure over the entire range. This was not by any means a conclusive consideration because it has been my experience that characteristic features have a tendency to become smeared out with decreasing pressure. The interpretation of a transition was made certain by the volumetric analysis, which showed a small volume discontinuity. This is one of the few examples where the shearing method has given less definite indications than the volume method; as already remarked there is no reason why the shearing method should not sometimes fail altogether.

Lanthanum. The original material was massive metal, obtained from Mackay, and said to be of about 98 percent purity. This shows distinct breaks with an increase of slope of between two- and threefold, both with increasing and decreasing pressure, at a mean hydrostatic pressure of 12,000 and a mean shearing stress of 700 kg/cm². It is therefore probable that there is a transition near this point. Measurements had been previously made to 12,000 both of compressibility and of electrical resistance without disclosing any transition. Not enough material was available for a volumetric analysis to high pressures. Beyond the transition, the curve of shearing force is concave toward the pressure axis, reaching 3100 kg/cm² at a hydrostatic pressure of 50,000.

[3] P. W. Bridgman, Proc. Am. Acad. **64**, 62 (1929).

Cerium. This has already been found to be polymorphic, the transition pressure at room temperature being about 7500 kg/cm². The shearing measurements showed a very sharp break, with decrease of slope practically to zero, at a mean hydrostatic pressure of 13,000 and a mean shearing stress of 2300 kg/cm². I think there can be no doubt that the transition is the same as found before; the rather unusual feature is the large effect of the shearing stress on the mean hydrostatic pressure of transition. The high pressure modification has, at the transition point, a lower shearing strength than the low pressure modification. Beyond the transition, the shearing strength rises, at first convex toward the pressure axis, then a point of inflection and reversal of curvature, reaching a maximum shearing strength of 3800 kg/cm² at 50,000.

Erbium. The original material was the powdered metal, obtained from Mackay, and must have contained a fairly large quantity of the oxide. There was much self-welding of the powder after the run; this method may perhaps make it possible to get the massive metal from the powders of some of the other rare earths. There was a comparatively small break in the curve of shearing force, with decreasing slope, at a mean hydrostatic pressure of 10,000 kg/cm² and a mean shearing stress of 900 kg/cm². It is perhaps possible, although I do not think it highly probable, that this break may mean a transition.

To a not bad first approximation, the shearing force is linear against pressure over the entire range, rising to 6400 kg/cm² at the maximum pressure of 50,000.

Thallium. There are two distinct breaks, both with increasing and decreasing pressure. The transition will be discussed in much greater detail in the volumetric paper. It is unusual that the pressure of transition is here markedly depressed by shearing stress, instead of being raised, as in the case of cerium, for example. The mean shearing strength at the transition was only 350 kg/cm², thallium being a very soft metal. The curve of shearing strength rises more rapidly beyond the transition, the high pressure form having the higher shearing strength, and at 50,000 reaches 1100 kg/cm².

Bismuth. Results for this have already been shown in Fig. 3 and details will be given in the volumetric paper. Modification III has a much lower shearing strength than I, whereas the high pressure modification IV has a considerably higher strength than III. The shearing strength of IV at 50,000 is 1660 kg/cm².

Thorium. The material was obtained from massive 4-mm rods of high purity from the Westinghouse Lamp Works. Four sets of experiments were made; the first three with the original apparatus gave definite evidence of breaks, but the sharpness of the results was obscured by friction in the apparatus, and there was also trouble from breaking of the pistons. The last experiment with the final frictionless apparatus confirmed the provisional results. There are two distinct breaks, both with decrease of slope, so that the high pressure modification must have a lower shearing strength than the low pressure modification. The breaks occur at a mean pressure of 12,000 kg/cm² and a mean shearing strength of 2500 kg/cm². Previous measurements of compressibility and electrical resistance under pure hydrostatic pressure had shown no transition to 12,000. The exploration under pure hydrostatic pressure has not been extended further. Beyond the transition point the shearing stress increases nearly linearly with pressure, reaching 5500 kg/cm² at 50,000.

Tin. This is one of the very soft metals; the shearing was throughout surprisingly easy and also perfectly smooth. There should be some commercial use in bearings subject to very high pressures. There is a distinct break in the curve of rotating force, with decrease of slope, at the same normal pressure, 10,000 kg/cm², both with increasing and decreasing pressure. The shearing force is 230 kg/cm² at the break. Previous measurements of compressibility and electrical resistance have shown no polymorphic transitions up to 12,000, and volumetric analysis by the new method showed nothing up to 50,000. It may be, therefore, that this is not an ordinary sort of transition. The change of slope is such that a possible explanation would be slippage on a new set of planes. Beyond the break the curve is slightly S shaped, with a maximum hysteresis between ascending and descending branches of

about 6 percent. The shearing strength at 50,000 was 770 kg/cm².

Yttrium. The shearing curves show a break which possibly may mean a transition. This is doubtful however, so that I have preferred to give it in the next section, where fuller details will be found.

Praseodymium. This was material of high purity for which I am much indebted to Dr. H. C. Kremers. Initially the shearing curve rises steeply, as would be expected of one of the harder metals. Near 10,000 kg/cm², however, where the shearing force is 750 kg/cm², there is a rapid decrease of slope, and the curve runs nearly horizontally up to nearly 30,000, where it turns again and rises rapidly to a shearing force of 2240 kg/cm² at 50,000. The same essential features are retraced with decreasing pressure, but with considerable hysteresis and rounding of the corners. This is one of the more striking of the transitions found, with a very drastic change of properties from a comparatively hard metal at low pressures to a modification stable at high pressures which is among the softest of those found.

B. Elements without breaks

We turn now to those elements which show no breaks and hence probably have no polymorphic transitions. The arrangement here is in order of atomic weight.

Beryllium. The rotation was perfectly smooth. The curve of shearing force against pressure was slightly S shaped, that is, at first convex toward the pressure axis, then a point of inflection and finally concavity, with very little hysteresis. The shearing strength at 50,000 was 7400 kg/cm².

Boron. The original material was amorphous powder, which experienced no appreciable self-welding. This was the hardest and most brittle of all the elements tried; rotation was accompanied by much jumping and loud snapping. In order to save the steel anvil, only a few readings were made with increasing pressure. Rotating force against pressure is convex toward the pressure axis for the entire range. The shearing force at a pressure of 50,000 kg/cm² was 18,000 kg/cm². As already remarked, the figure 18,000 thus sets a lower limit for the shearing strength of the hardened steel pistons.

Carbon. A rather large number of experiments were made with graphite. A number of these experiments were made with preliminary forms of apparatus before the evolution of the final form. Always I had a hope that the permanent change to diamond might be induced, but such never occurred. In the final measurements both single crystal graphite, with the cleavage planes parallel to the faces of the piston, and ordinary massive Acheson graphite were used. As already remarked, rotation of the single crystal was at first surprisingly easy, until the crystal structure was broken up. Then it settles down into a final behavior like the ordinary massive graphite. Up to a certain pressure, in the neighborhood of 12,000 kg/cm², rotation is smooth and metallic; at this point there is a break in the curve with the beginning of snapping and jumping, which gets steadily more violent, until at the maximum pressure the jumps are 50 percent of the average reading. The graphite acts like an abrasive on the steel. The graphite itself emerges as a fine powder with no self-welding. The curve of rotating force against pressure is nearly linear, slightly S shaped in the normal direction, with a maximum width of the hysteresis loop averaging about 5 percent of the maximum. The shearing strength at the maximum pressure of 50,000 is 10,000 kg/cm². Explorations were also made by the volumetric method, but no discontinuities were found up to 50,000.

Sodium. The curve of rotating force for sodium is highly remarkable. At the lowest pressures, rotation was so easy as to be almost below the limits of measurement with the particular dimensions of apparatus; this is as is to be expected because of the great softness of sodium. But the curve rapidly rises at an accelerated pace, and is convex toward the pressure axis over its entire extent. This must mean a very unusually great increase of shearing strength with pressure. With decreasing pressure there is unusually large hysteresis, the maximum width of the loop being nearly 20 percent of the maximum effect. This perhaps is not surprising because the irreversible geometrical phenomena must be unusually prominent with so soft a material. The general aspect of the curve is much like that already found for lithium, with the difference that the sharp break in direction of lithium is here smeared out into a

region of unusually great curvature. The maximum shearing strength at 50,000 was 5200 kg/cm², against 3000 for lithium, and this in spite of the fact that initially sodium is much softer than lithium. Behavior under shearing stress therefore appears to be another phenomenon in which the relative position of the alkali metals becomes reversed at high pressures; I have already found that the order of the melting points and of the thermal expansions reverses at high pressures.

Magnesium. This metal behaves more like what our preliminary discussion suggested we might naturally expect than nearly any other substance. Shearing is perfectly smooth, with very little difference between maximum and minimum rotating force at any fixed pressure; furthermore there was very little hysteresis between increasing and decreasing pressure. In the very early stages the curve of rotating force is slightly convex toward the pressure axis, then there is an inflection at about 2000 kg/cm² normal pressure, and from here on concavity, with a closer approach to a horizontal asymptote than usual. Thus at 12,000 kg/cm² pressure the shearing strength was 840 kg/cm², and at 24,000, 980. In the final measurements, the 0.5-inch pistons were used and pressure was not carried higher than 24,000, but in a couple of preliminary experiments it was found that there is probably no transition up to 50,000.

Aluminum. This gives perfectly smooth rotation, with little variation of force and little hysteresis. There was some welding of the aluminum to the steel. The curve of rotating force is composed approximately of two linear parts, joined by a region concave toward the pressure axis. At 12,000 pressure the shearing strength was 1100 kg/cm², and at 50,000, 3200.

Silicon. The initial material was massive silicon of high purity which I obtained 10 years ago from the National Physical Laboratory at Teddington. Rotation was accompanied by grinding noises and by jumping, from the lowest pressures over the entire range. There was no self-welding, but the silicon was compressed into an apparently coherent cake, which fell apart on the slightest handling. There was much abrasive action on the steel. Rotating force against pressure is gently concave upwards over the entire range, with a shearing strength of 9000 kg/cm² at 50,000. The measurements were repeated with essentially the same results.

Phosphorus. In the qualitative part I have already described how violet phosphorus is transformed by shearing into the denser variety of black phosphorus; this is the only method yet found for changing violet to black. Measurements on black phosphorus disclosed no further transitions up to 50,000. Black phosphorus under atmospheric conditions is a greasy feeling substance, much like graphite, but even softer. The rotation was not quiet, but from almost the lowest pressure there was continuous snapping, and there was distinct abrasive action on the steel pistons. At any fixed pressure, the steady readings corresponded to the maximum rotating force, with momentary jumps to lower values. With increasing pressure the curve of rotating force is gently concave upward; the decreasing curve shows much hysteresis, and is of the conventional S shape. The shearing strength at 50,000 was 8300 kg/cm².

Sulfur. A great many measurements were made on sulfur, both with the volumetric and the shearing apparatus, because it was my strong conviction that there must be a metallic form of sulfur analogous to black phosphorus; this, however, was never found. Both ordinary crystalline sulfur and the amorphous modification obtained by quenching hot liquid sulfur into water were investigated. There are still some unsettled questions as to what happens. On one occasion, starting with amorphous sulfur as the initial material, there was quite a violent detonation on rotating at 50,000. On another occasion, starting with crystalline sulfur, there was a mild detonation at 25,000 on the seasoning application of pressure, but from here on everything went smoothly. On another occasion with crystalline sulfur as the initial material, the entire shearing program was carried through with no detonation. I am inclined to think that the detonations are due to the presence of a greater or smaller amount of oxygen adsorbed onto the sulfur, since the qualitative experiments showed an unusual instability of the oxides. At any rate, I think there can be no doubt, from the appearance of the end product, that the original crystalline material is converted by shearing force into the rubber-like, sticky,

amorphous variety. The volumetric experiments with nearly pure hydrostatic pressure showed no such transformation.

Shearing of sulfur was not smooth throughout, but beyond 25,000 was accompanied by scraping noises and slight chattering. The final curve is an unusually close approach to a straight line, with very gentle concavity toward the pressure axis, and a hysteresis loop with a maximum width of not more than 5 percent of the maximum effect. The shearing strength at 50,000 was 7000 kg/cm², enormously higher than the shearing strength under normal conditions.

Titanium. The original material, for which I am indebted to the Research Laboratory of the Westinghouse Electric Company, was said to contain about 5 percent impurity; it was very brittle, with a glass-like fracture, which reminded one more of the intermetallic compounds than of a metal. In spite of this, it permitted shearing much more quietly than anticipated, there being only very little snapping or jumping. There was distinct abrasive action on the steel parts. The curve of rotating force is convex toward the pressure axis over the entire extent, both with increasing and decreasing pressure, with a maximum width of the hysteresis loop of 10 percent of the maximum effect. The shearing strength at 50,000 was 13,000 kg/cm², which is thus among the highest.

Chromium. The material was from Kahlbaum, made by the Goldschmidt process, from the Laboratory stock, and was evidently made a number of years ago. In spite of its brittleness, shearing was perfectly smooth and quiet, with little variation of force, and slight width of the hysteresis loop. There was, however, marked abrasive action on the steel. The curve of rotating force is gently concave toward the pressure axis, with a slight initial hook. The shearing strength under 50,000 was 12,300 kg/cm².

Iron. This material was the purest Armco iron. It rotated perfectly smoothly. Up to a pressure of 25,000 the curve of rotating force against pressure was much more markedly S shaped with increasing than with decreasing pressure; above 25,000, the curve is nearly linear and without hysteresis. The shearing strength at 42,000 (the maximum in this experiment) was 10,600 kg/cm²; in view of the softness of the original material it was a surprise that this figure was so high.

Nickel. This sheared perfectly smoothly. The curve with increasing pressure was much more notably S shaped than with decreasing pressure, with a point of inflection near 30,000. Above 30 000 there is marked concavity toward the pressure axis. The shearing strength at 50,000 was 8700 kg/cm².

Cobalt. This sheared perfectly smoothly. The curve of rotating force in broad outline is gently S shaped with little hysteresis. Near 40,000 there appears to be a slight break in direction, with decrease of slope. This was found both with increasing and decreasing pressure, and I suspect that it might have been better to list this substance in the first group, among those with polymorphic transitions, but marked doubtful. The shearing strength at 50,000 was 6300 kg/cm². Notice the decrease in shearing strength in the series Fe, Ni, Co, or for that matter in the series Ti, V, Cr, Mn, Fe, Ni, Co.

Copper. Measurements were made both with commercial copper and with 99.999 percent electrolytic copper, with no essential difference. Shearing is perfectly smooth; the hysteresis is rather larger than usual, and rather less with electrolytic than with commercial copper. The curve of rotating force is convex toward the pressure axis over nearly its entire extent, with a slight hook near the origin. The shearing strength is 4700 kg/cm² at 50,000.

Germanium. The material was highly purified, for which I am indebted to Professor Dennis of Cornell. Shearing was not smooth, and there was so much fluctuation in the force that it was difficult to estimate what the best mean value was, but paradoxically there was no noise. The steel pistons were hardly touched, and the general behavior was surprising in view of the pronounced glass-like nonmetallic character of the original material. The curve of rotating force is gently concave toward the pressure axis over the entire extent. The shearing strength at 50,000 was 5700 kg/cm².

Arsenic. This material was originally from Kahlbaum. The first set-up was with powdered material that had been exposed to the air for several days. This detonated at 20,000 on the first application of pressure, doubtless due to the

oxide. The next set-up was with freshly cleaved flakes from a single crystal that I had left from previous work. Even with this there was a very slight detonation at 30,000. This probably had the effect of eliminating the slight amount of oxygen; the measurements were continued with regular results, and at the conclusion a residue of metallic arsenic was found as expected. Shearing was not smooth, but there was snapping and jumping, continually getting more violent beyond 5000. There was no abrasive action on the pistons, which were practically untouched. The curve of rotating force is gently S shaped, with the point of inflection at 5000, and little hysteresis. The shearing strength at 50,000 was 11,200 kg/cm². With so high a figure as this one might expect more action on the steel.

Previous work with single crystal arsenic[4] had shown some anomalous effects associated with one of the directions of the crystal. One might have expected some reflection of this in the shearing experiments, but none was found. One might also have expected high pressure polymorphism, analogous to the polymorphism of bismuth and the probable polymorphism of antimony.

Selenium. A number of different measurements were made on this; it is an interesting substance both because of the possibility of an irreversible transition like black phosphorus, and also because it normally exists in two forms, an amorphous and a metallic form with large difference of density. The amorphous material used in these experiments was amorphous material from Kahlbaum; the metallic was material purified in this laboratory several years ago by Dr. W. E. Danforth, Jr., by very slow distillation over a period of several weeks. No appreciable difference could be found in these experiments between the two modifications. In both cases shearing is smooth over almost the entire range, there being slight squeaks of protest only occasionally. The curves are gently concave toward the pressure axis, with only a slight hook at the origin, and with very small hysteresis. The shearing strength at 50,000 was found to be 5500 kg/cm² for the metallic and 5600 for the amorphous variety, essentially the same. Dr. Jacobs was kind enough to make an x-ray examination of the various products. The metallic showed at the conclusion of the experiments the same lines and of very nearly the same sharpness as the initial material. This result is of itself of much interest as showing that the grain size even under such extremely drastic conditions is not reduced below the value necessary to give fairly well-defined x-ray pictures. The amorphous material, on the other hand, showed a distinct alteration after the shear, there now appeared the lines of the metallic selenium, but less sharp. It would appear, then, that amorphous selenium is converted into metallic by shearing. This conversion must take place at a very low shearing force, because in the endeavor to locate this transition, which of course was expected, I made the measurements on amorphous selenium with no initial seasoning, and in spite of this found no evidence of change at the lowest measured point, where the hydrostatic pressure was 4000 and the shearing force 400 kg/cm². On the other hand, the volumetric exploration showed no transition of amorphous to metallic selenium up to 50,000.

Yttrium. The material was finely powdered metal from Mackay. Shearing was quiet up to 35,000, from here on there was slight noise and jumping. The powder was self-welded by the shearing into a coherent disk. To a first approximation the curve of shearing strength against pressure is linear, slightly concave toward the pressure axis over the entire range, and with hysteresis rising at the maximum to 10 percent of the maximum effect. The shearing strength at 50,000 was 4300 kg/cm². Superposed on this there is a small but definite break, both with increasing and decreasing pressure, at a mean pressure of 16,000 kg/cm² and a mean shearing stress of 1600 kg/cm². It is not unlikely that the breaks mean a transition.

Zirconium. This material was originally from Eindhoven, left from previous measurements of compressibility and resistance.[5] It sheared perfectly smoothly. The curve of rotating force with increasing pressure was markedly S shaped; the curve was also S shaped with decreasing pressure, but not to so great an extent, with a maximum width of the hysteresis loop of 15 percent of the

[4] P. W. Bridgman, Proc. Am. Acad. **68**, 39 (1933); **68**, 109 (1933).

[5] P. W. Bridgman, Proc. Am. Acad. **63**, 347 (1928).

maximum effect. The shearing strength at 50,000 kg/cm² was 4400 kg/cm². This is perhaps not as great as might be expected in view of the initial hardness. The curvature is greater than usual, with a closer approach than usual to the ideal conditions of shearing strength independent of pressure.

Columbium. Shearing was perfectly smooth. The curve of rotating force with increasing pressure was markedly convex toward the pressure axis over the entire range; the curve with decreasing pressure was slightly S shaped, with a maximum width of the hysteresis loop of 20 percent of the maximum effect. The mean curve for both increasing and decreasing pressure is also markedly convex toward the pressure axis over the entire range. The shearing strength at 50,000 was 9000 kg/cm².

Molybdenum. Shearing was perfectly smooth. Both increasing and decreasing curves were convex toward the pressure axis over the entire range, with a maximum hysteresis of 10 percent of the maximum effect. The shearing force at 50,000 was 12,100 kg/cm², one of the highest, as might be expected.

Ruthenium. Shearing was perfectly smooth; the pistons were burnished after the run, but there was no abrasive action. The curve of rotating force was slightly S shaped both with increasing and decreasing pressure, with a hysteresis amounting to 7 percent at the maximum. The shearing force at 50,000 was 9600 kg/cm².

Rhodium. Shearing was perfectly smooth; the pistons were burnished with some welding of the rhodium to them. The curve of rotating force was nearly linear over its entire extent, with a slight hook at the origin, and maximum hysteresis of 9 percent. There were various slight irregularities in the curve, which probably were of no significance. The shearing force at 50,000 was 8900 kg/cm².

Palladium. Shearing was perfectly smooth, with nearly constant readings at any one pressure. The curve of rotating force was markedly concave toward the pressure axis over the entire range, with a maximum difference between increasing and decreasing readings of 4 percent. The shearing strength at 50,000 was 5600 kg/cm² and at 25,000, 4100. Notice the same decrease of shearing strength in the series Ru, Rh, Pd as in Fe, Ni, Co.

Silver. Shearing was perfectly smooth, but with more variation of the force than usual during the process of attaining a steady value. The curve of rotating force with increasing pressure was slightly concave toward the pressure axis with a slight hook at the origin. The decreasing curve showed a rather large drop on starting back, which probably is of no significance because it was not found with the first apparatus. The shearing strength at 50,000 was 4700 kg/cm².

Indium. This is one of the very soft metals, and the rotating force was throughout very small. The increasing and decreasing curves differed only slightly in absolute terms, but cross a couple of times. The crossing is probably without significance, because with the first apparatus crossing was also found, but in the reverse order. Both pieces of apparatus gave mean curves gently convex toward the pressure axis over their entire extent. The shearing strength at 50,000 was 750 kg/cm².

Tantalum. Shearing was perfectly smooth. There was distinct welding to the steel pistons and tearing of the steel surfaces. The curve of rotating force is very markedly S shaped with increasing pressure, with the region of pronounced and maximum curvature near 20,000. The S shape was not so prominent with decreasing pressure. The maximum width of the hysteresis loop was 8.5 percent of the maximum effect. The shearing strength at 25,000 was 7700 kg/cm² and at 50,000, 11,500.

Tungsten. Shearing was perfectly smooth. There was considerable scratching of the pistons, and the tungsten lost its original coherent form and was broken up into small flakes, showing little if any self-welding under these conditions. This is not surprising in view of the high melting point. The curve of rotating force was markedly convex toward the pressure axis over the entire extent with increasing pressure, but had a slight S shape with decreasing pressure, and a maximum hysteresis of 18 percent. The shearing stress at 50,000 was 12,700 kg/cm², one of the highest, as was to be expected.

Rhenium. The material was finely powdered metal from Mackay, of unknown purity. Shear-

ing was quiet, with much variation of force. Self-welding takes place to a very appreciable extent, the end-product consisting of flakes of coherent metal. The curve of shearing force is gently convex toward the pressure axis over the entire length, with a maximum difference between ascending and descending branches of 3 percent. The shearing strength at 50,000 was 7500 kg/cm².

Osmium. The original material was some electric lamp filaments, 0.020 inch in diameter, obtained a number of years ago from the General Electric Company, a product of the early extensive experimentation to find the best material for filaments. These filaments were highly crystalline and very brittle; they were broken into appropriate lengths and laid closely side by side on the pistons. Rotation was never smooth, but was only accomplished with noisy protest, and there were violent fluctuations in the rotating force. The pistons were deeply abraded. The curve of rotating force was almost linear against pressure, with slight convexity toward the pressure axis, and with inappreciable hysteresis. The shearing force at 50,000 was 17,400 kg/cm², nearly as high as for boron.

Iridium. The material was lengths of wire 0.030 inch in diameter, which had been previously used in compressibility and resistance measurements, laid side by side underneath the pistons. Rotation was perfectly smooth. There was no self-welding of the pieces of wire, and the pistons were burnished rather than scratched. The curve of rotating force is almost exactly linear, with very slight concavity toward the pressure axis, and a slight hook near the origin. Except at the very lowest pressure, readings with increasing and decreasing pressure were indistinguishable. The shearing stress at 50,000 was 8400 kg/cm²; one might expect a figure near the top because of the proverbial hardness of iridium.

Platinum. Shearing was perfectly smooth, with little variation of force. The curve of rotating force was markedly concave toward the pressure axis with a slight hook at the origin. Beyond 15,000 the readings with increasing and decreasing pressure were indistinguishable; the greatest difference was at 6000, where the hysteresis amounted to about 8 percent of the maximum effect. The shearing stress at 50,000 was 5800 and at 25,000, 4100 kg/cm². Notice again the striking decrease in the series Os, Ir, Pt, and also the progression in curvature.

Gold. Shearing was perfectly smooth with little variation of force. The curve was markedly S shaped with increasing pressure, but much less pronounced with decreasing pressure, in fact the two curves cross, with a maximum difference between increasing and decreasing readings of 13 percent of the maximum effect. The mean curve is gently concave toward the pressure axis over its entire length. The shearing stress at 50,000 was 4500 kg/cm². The shearing strength of Cu, Ag, and Au at 50,000 are almost identical; the rather large initial differences, shown most strikingly by the great malleability of gold, thus are wiped out at high pressures.

Lead. This is one of the weakest and softest of the metals and gave low shearing forces as would be expected. Shearing was throughout perfectly smooth; the force rises approximately linearly with pressure, reaching 710 kg/cm² at 50,000 pressure. The existence of no polymorphic transition was checked by a volumetric exploration.

Uranium. This was massive material, obtained through Mackay, originally prepared by the late Professor James of New Hampshire State College, and said to be of high purity. It was not perfectly homogeneous in appearance, however, but seemed to contain some sort of inclusion. Two runs were made, the first sample appearing to be more homogeneous than the second. The shearing of the first was perfectly smooth, but the second showed a little jumping. The shearing strengths at 50,000 were, respectively, 8900 and 10,200, the difference being in the direction to be expected. In both cases the curves of rotating force were slightly S shaped, with little difference between increasing and decreasing readings.

Discussion

It is interesting to summarize the results with respect to the ease with which shearing takes place. It is almost always the case that a typical metallic structure, face-centered cubic, body-centered cubic, or hexagonal close packed, permits plastic flow quietly. Apparent exceptions were osmium and vanadium, but it is highly

questionable in view of the very brittle character of the original material whether these were sufficiently pure. Other apparent exceptions are Li, Sr, Ce, and Er, but all these have been shown probably to have transitions at high pressure, and shearing loses its smoothness only at high pressures in these cases. It is therefore probable that in these cases the change in the character of the shearing is to be attributed to the transition, and in fact this change in character affords additional presumptive evidence of the reality of the transition. We may draw the further conclusion that the high pressure forms are probably of lower symmetry than the low pressure forms. Lithium is particularly interesting because of its extreme softness. Yttrium does not shear smoothly; its crystal structure appears not to be known. The substances which make the greatest fuss on being sheared are the typical nonmetallic elements B, C, Si, black P, Ge, and As. On the other hand, S, a thorough nonmetal, shears quietly, but we have seen that S probably changes to the amorphous rubber-like variety on shearing. The crystal structure is not completely determinative in this regard, because Bi and Sb both have As structure and shear quietly; but the properties of these are more metallic than of As.

There is no close correlation between smoothness of shearing and the numerical value of the resistance to shear.

In Table II are collected the values of one-half the tensile strength, taken from the last edition of Landolt and Börnstein, and also the shearing stress supported at the maximum pressures reached in the experiments of this paper.

TABLE II. *Comparison of shearing strength at 50,000 kg/cm² and one-half tensile strength at atmospheric pressure.*

Substance	Shearing Strength at 50,000 (kg/cm²)	½ Tensile Strength at Atmos. Press. (kg/cm²)	Substance	Shearing Strength at 50,000 (kg/cm²)	½ Tensile Strength at Atmos. Press. (kg/cm²)
Al	3,200	300	Mo	12,100	3,500
Pb	650[1]	90	Ni	8,700	2,500
Cd	860[2]	325	Pd	5,600	1,050
Ca	1,800	250	Pt	5,800	950
Co	6,300	1,250	Ag	4,700	650
Fe	10,600	1,250	Tl	11,000	45
Au	4,500	700	W	12,700	7,500
Cu	4,900[3]	1,100	Zn	2,000	750–1,000
Mg	980[4]	1,000	Sn	770	125

[1] At 23,000; [2] at 10,000, [3] at 40,000; [4] at 23,000.

Except in the case of Mg, where I believe that there must be a misprint in the tabulated value, the shearing stresses withstood here are higher by a factor of several-fold than one-half the tensile strength, showing how profound an effect high pressure may have on shearing strength.

High shearing stress means high shearing strain. A pure shear is accompanied by an elongation in one direction equal numerically to one-half the shearing strain, and a compression of equal numerical magnitude at right angles. It follows that the actual separation of atoms or molecules under these conditions is much greater than the maximum attainable under ordinary tensile test conditions, where the limit is set by rupture. If the elongation is great enough, one might expect the molecules to be actually torn apart, and to regroup themselves in configurations of greater stability. It may well be that something of this sort plays a part in some of the cases of chemical instability described in the first part. One might perhaps be disposed to expect the effect to be particularly important among the organic compounds, the elastic constants of which are usually low, which means in general a large deformation. Or particular classes of compound may be particularly sensitive to distortion; one suspects that the oxides may be such a class.

There are doubtless other important factors which enter into the chemical effects. Under the disorganized plastic flow which accompanies shear in these experiments every sort of conceivable regrouping must be taking place, thus allowing a chance for any phenomenon to take place which is thermodynamically possible. One would expect phenomena of inhibition, such as subcooling, or the failure under ordinary conditions of reactions like $2H_2+O_2=2H_2O$, to be entirely suppressed. An example of this sort taken from the polymorphic transitions described above is that of tellurium; this transition takes place at room temperature under shearing stress, but volumetric analysis discloses it only at higher temperatures, although an extrapolation of the results indicates that it should be found at room temperature if it were not for viscous resistance. Allied with this effect is the fact that under the grinding action incident to plastic flow the reactants are brought into such intimate

contact that reactions otherwise suppressed take place. The reaction between SiO_2 and Al must have a large element of this effect in it. Finally, there may be the simple displacement by shearing stress of the temperature and pressure at which the thermodynamic potential of the two reactants are equal, thus allowing the possibility of bringing a reaction or transition into the attainable range which ordinarily would be outside it. There are a couple of examples above where the displacement seems to be as much as 10,000 kg/cm^2.

Results of much geophysical interest may be anticipated from a study of more complicated systems than those examined above. Polymorphism may be expected to be a common phenomenon under the high pressures in the interior of the earth. The volume changes associated with polymorphic transitions combined with the greatly enhanced shearing strength under pressure of practically every substance must afford opportunity, at least locally and temporarily, for the development of high shearing stresses in the interior of the earth, under the action of which novel chemical reactions may well occur.

Note added October 30. Additional experiments to elucidate the reason for the detonations described in the qualitative section make it appear that in at least some cases the primary cause of the detonation is mechanical. Apparently certain substances have such a relation between coefficient of friction, plastic flow stress, normal pressure, and film thickness that when the pressure reaches a critical value the film may become mechanically unstable and be violently expelled, having as a secondary effect local, very considerable increases of temperature. The subject is evidently complex and a single type of explanation will probably not apply in all cases.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Protons from the Disintegration of Lithium by Deuterons

It was found in this laboratory[1] that lithium bombarded with deuterons yields β-rays with a continuous distribution in energy extending to 10.5 ± 1.0 MEV and having a half-life of 0.5 ± 0.1 second. In order to account for these β-rays the following reactions were suggested:

$$_3Li^7+{}_1H^2\rightarrow{}_3Li^8+{}_1H^1, \quad (1)$$

$$_3Li^8\rightarrow{}_4Be^8+{}_{-1}e^0. \quad (2)$$

We have recently attempted to determine the range and energy of the protons accompanying the formation of radioactive Li^8. A target of lithium metal was so disposed that disintegration particles could be admitted through a copper foil into a cloud chamber operating at a pressure of three atmospheres. Diaphragms between the target and the window limited observation to particles making an angle of $90°\pm5°$ with the incident ions. Ethyl alcohol was employed in the chamber and the stopping power of the resulting air-vapor mixture was computed from the measured chamber pressure and the vapor pressure of alcohol at the operating temperature. A polonium alpha-particle source installed in the chamber served to check the computed results. The stopping power of the copper foil (9.6 mg/cm^2) was found to be 4.7 cm by measuring the residual range of the alpha-particles yielded by bombarding lithium with protons. The stopping power for alpha-particles and protons of other ranges was computed from the data given by Mano[2] and the necessary corrections incorporated in the ranges given in Fig. 1.

The distribution in range of the particles resulting from the disintegration of lithium by 700 kv (peak) deuterons is shown in Fig. 1. The "extrapolated" ranges of 31.7 ± 0.5 cm, 13.8 ± 0.7 cm, and 8.9 ± 1.0 cm, respectively, for the longer range protons and two alpha-particle groups are in good agreement with the ranges which have been measured at Cambridge.[3] The group of particles at 26 ± 1 cm has not been reported previously. The energy of protons of this range is 4.3 ± 0.1 MEV. If the particles are produced in the manner indicated by reaction (1) then the energy released in the disintegration is $Q=4.3$ MEV and the masses of Li^8 and Be^8 are on the Bethe scale:

$$Li^8=8.0185,$$
$$Be^8=8.0072=2He^4+0.5\pm1.0 \text{ MEV}.$$

Possible contamination effects could arise from the presence of protons in the ion beam or from oxygen, nitrogen, deuterium, or carbon in the target. No particles corresponding to the 26-cm group are known to be emitted in the transmutation of the last-named elements. We have found correspondence within a factor of two or three between the number of electrons from reaction (2) and this second proton group.

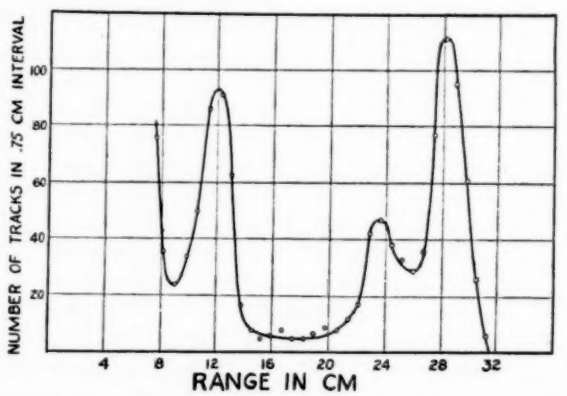

FIG. 1. Distribution in range of alpha-particles (short range groups) and protons (long range groups) emitted in the disintegration of lithium by 700-kv peak deuterons.

Oliphant, Shire and Crowther[4] employing 160-kv deuterons have reported protons from a thin Li^6 target but not from Li^7 targets of equal thickness. The fact that the yield with the latter targets would be but 2 percent of that from the former may account for their results. If the 26-cm protons are emitted in the transmutation of Li^6 then they may accompany the formation of excited Li^7 and the subsequent emission of a γ-ray. The 30.5 ± 1.0-cm protons observed by Cockcroft and Walton[5] at 500 kv extended over a range of 10 cm, a fact consistent with the existence of two unresolved groups of particles.

L. A. DELSASSO
W. A. FOWLER
C. C. LAURITSEN

California Institute of Technology,
October 29, 1935.

[1] Crane, Delsasso, Fowler and Lauritsen, Phys. Rev. **47**, 971 (1935).
[2] Mano, J. de phys. et rad. **5**, 628 (1934).
[3] Oliphant and Cockcroft, Int. Conf. on Physics, 1934.
[4] Oliphant, Shire and Crowther, Proc. Roy. Soc. **A146**, 922 (1934).
[5] Cockcroft and Walton, Proc. Roy. Soc. **A144**, 704 (1934).

On Dirac's Equation in Rotating Systems

In a previous publication[1] two relations were given (Eqs. (25) and (35)) which expressed Dirac's equation in a rotating frame of reference. We now give a third one which is of interest. The matrices

$$\bar{\bar{\gamma}}_k=\mathring{\gamma}_k \ (k=1, 2, 3), \qquad \bar{\bar{\gamma}}_4=\mathring{\gamma}_4+i\omega'(y\mathring{\gamma}_1-x\mathring{\gamma}_2)$$

satisfy the commutation relations exactly, and lead to the equation

$$\bar{H}\chi\equiv[-\pi_4+\alpha\cdot\pi+mc\beta-\omega' L_z-\tfrac{1}{2}\hbar\omega'\sigma_z]\chi=0.$$

$\bar{H}'$ is connected with H' and $\bar{H}'$ [2] by the spin transformations

$$\bar{H}' = Q^{-1}\bar{H}'Q, \qquad H' = R^{-1}\bar{H}'R,$$

where $Q = \cos \tfrac{1}{2}\omega t - i\sigma_Z \sin \tfrac{1}{2}\omega t,$

$R = 1 + \tfrac{1}{2}\omega'(x\alpha_y - y\alpha_x) + \tfrac{1}{8}\omega'^2(x^2+y^2).$

Q is exact, R is accurate to second-order terms in ω'. It follows that $S = QR$, $H' = S^{-1}\bar{H}'S$.[3]

GABRIEL HELLER

Talladega College,
Talladega, Alabama,
October 25, 1935.

[1] O. Halpern and G. Heller, Phys. Rev. **48**, 434 (1935). The present note follows the notation of this reference.
[2] H' denotes the covariant form of the Hamiltonian, $H' = \beta H$.
[3] The accents were erroneously missing in Eq. ($\bar{7}$a), reference 1.

The Ionosphere, Sunspots, and Magnetic Storms

During recent years there has been much published speculation concerning the relations between the condition of the ionosphere, radio transmission, and the phenomena of magnetic storms and sunspots. It has been observed that it is difficult to maintain high frequency communication over certain paths during magnetic disturbances and there is some evidence that the maximum useful frequency is lower during the minimum of a sunspot cycle than during the maximum. The following striking phenomena which corroborate and extend these data, have been observed by us at the National Bureau of Standards.

The normal-incidence noon value of $f_{F_2}{}^x$[1] which had been below 7500 kc/sec. during the summer, rose gradually during October, attaining the hitherto unobserved peak of 12,600 kc/sec. on October 21. This period of high $f_{F_2}{}^x$ approximately coincided with a period of high sunspot activity. On October 21 a series of magnetic disturbances set in. These were intermittent and at first mild, but reached considerable sustained intensity on October 23 and 24. The $f_{F_2}{}^x$ decreased slightly from October 21 to October 23, dropped very decidedly to 6400 kc/sec. on October 24, then rose slowly during the following days, as shown in Fig. 1. The noon $f_{F_2}{}^x$ was representative of the day values. The F critical frequencies during the night of October 24–25 were below those obtained on the preceding nights but not as much of a decrease as for the day values occurred.

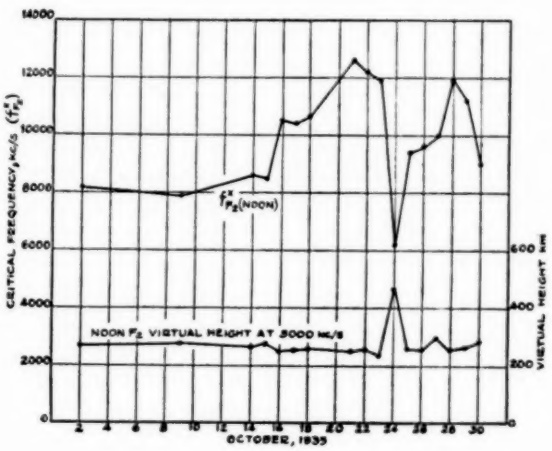

FIG. 1.

The F_1 critical frequencies were sharply defined on October 24. Both components were present. During the other days of this period $f_{F_1}{}^0$ was blunt and poorly defined as is normal for this season, and the extraordinary ray was not observed. The high values of $f_{F_2}{}^x$ were accompanied by low virtual heights of the F_2 region and *vice versa*, as shown in Fig. 1. The sharply defined F_1 critical frequencies seemed to be produced when the F_2 region rose and separated from the F_1. This is a normal summer day condition such as prevailed before the F_2 critical frequencies rose in October.

The high critical frequencies were accompanied by excellent transmission conditions for frequencies up to 30 megacycles per second, the limit of the receiver available, and probably conditions continued good up to 40 mc/sec. On October 24, the day of the low critical frequencies, transmission conditions were not as good as on previous days, many transmissions which had been received regularly on previous days failed, and others were much weaker. The critical-frequency data indicated that the maximum useful transmission frequency on October 21 was about twice that of October 24. The F_2 ionization density found on October 24 was about 23 percent of that found on October 21.

No deviations from normal were observed for the F_1 critical frequencies or virtual heights. No unseasonable change was observed during this period in the conditions of the E region, which is the region usually controlling transmission at the ordinary broadcast frequencies (550 to 1500 kc/sec.).

Dr. E. O. Hulburt[2] has given a reasonable theory for the low ionization densities and great virtual heights of the F_2 region during summer days. According to this theory these conditions are caused by atmospheric expansion produced by heating. Similar conditions seem to exist during the latter part of a magnetic storm. The results given above then indicate the probability that some agency acting during magnetic storms, heats the F_2 region to values abnormal for the season, causing the atmosphere there to expand, and in this manner reduces the ionization density and increases the virtual height of this region.

The effect of the sunspot activity seems to be to increase the ionization density of the F_2 region. On the other hand, though magnetic disturbances are more frequent and intense during the active part of the sunspot cycle, some agency acting for short times during these periods serves to decrease the ionization density of the F_2 region much below normal and increase the height of this region much above normal.

S. S. KIRBY
T. R. GILLILAND
E. B. JUDSON
N. SMITH

National Bureau of Standards,
November 2, 1935.

[1] $f_{F_2}{}^x = F_2$ critical frequency, extraordinary ray, i.e., the highest radiofrequency which is returned to earth by the F_2 region of the ionosphere.
[2] Hulburt, Phys. Rev. **46**, 822 (1934). Terr. Mag. 193, June (1935).

Photography of the Third Harmonic of Hydrogen Chloride

The first photographic investigation of a vibration-rotation band of a diatomic molecule was that completed by Herzberg and Spinks[1] for the second harmonic of hydrogen chloride. At present a similar research is in progress on the third harmonic at 9153A. A thirteen-meter path of the gas has been found barely adequate to reveal a few lines in this band in the first order of a 6.4-meter grating, the dispersion being 2.6A/mm. Determination of wave-lengths has been made from standard iron arc lines in the second order.

Two groups of observers have reported results which permit the calculation of the wave number for the origin of the third harmonic according to the wave mechanics expression for a diatomic molecule published by P. M. Morse.[2]

$$\nu(n'-n'') = (n'-n'')[\omega_0 - x\omega_0(n'+n''+1)].$$

The groups are: (I) Herzberg and Spinks; (II) Colby, Meyer and Bronk,[3] also Meyer and Levin.[4] The values of the constants and the wave number of the band origin are tabulated below:

	(I)	(II)
ω_0	2989.00 cm^{-1}	2989.68 cm^{-1}
$x\omega_0$	51.65 cm^{-1}	51.90 cm^{-1}
x	0.01728	0.01736
$\nu(4\leftarrow 0)$	10,923.00 cm^{-1}	10,920.72 cm^{-1}

In the present research the wave number of the band origin has been determined to be 10,922.7 cm^{-1}. More complete results should be available as soon as the path length of gas has been doubled.

ALDEN P. CLEAVES
CHARLES W. EDWARDS

Duke University,
Durham, North Carolina,
October 29, 1935.

[1] G. Herzberg and J. Spinks, Zeits. f. Physik **89**, 474 (1934).
[2] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[3] Colby, Meyer and Bronk, Astrophys. J. **57**, 7 (1923).
[4] Meyer and Levin, Phys. Rev. **34**, 44 (1929).

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